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(I.C)

PRINCIPLES

OF

THEORETICAL

CHEMISTRY,

WITH SPECIAL REFERENCE TO THE

CONSTITUTION OF CHEMICAL COMPOUNDS.

BY

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PHILADELPHIA:
HENRY C. LEA.
1877.

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PREFACE.

THIS little book is intended to furnish the student with a simple statement of the fundamental principles of what is commonly called Theoretical Chemistry. The subject is, of course, not exhausted; many things have purposely been left out, either because they have not yet reached such a stage of development as to entitle them to a place among the fundamental principles, or because it was thought better to emphasize more strongly those principles which are treated. Should the reader miss anything which he expected to find, he will please carefully consider whether the grounds referred to are a sufficient excuse for the omission.

The imperfections that will be noticed are, partly at least, due to the imperfection of our knowledge on some of the subjects discussed. For instance, it seems to be impossible for us at present to treat the subject of Valence in such a way as to lead to satisfactory results, mainly for the reason that we know so little in regard to it. Whatever view of this property one may take, he will find some difficulties which he cannot surmount.

As for the value of the structural formulas, which are discussed at some length in the second part of the book, it need only be said that, if it be borne in mind what they are intended to represent, they are not quite so absurd as some chemists are just now trying to make us believe they are. These formulas certainly represent known facts in regard to the constitution of chemical compounds. They do not represent these compounds as a photograph, for example, represents a building; but rather somewhat in the same way that, in Physics, lines represent forces in their magnitude and direction. Take the formulas for what they are, and they have considerable value. Try to find in them the architectural plans of the chemical molecules, and they appear absurd. But it is very unjust to find fault with a thing for not doing what it never pretended to do, and what its originators have distinctly stated it could not do.

A careful study of this book will, it is believed, be of assistance in showing exactly upon what basis our conceptions of chemical constitution rest. Whether our ideas are good or bad, they deserve to be studied, for the simple reason that they are held by nearly all the working chemists of the day, and much of the work that is being done in the principal laboratories is a result of these prevailing ideas.

I. R.

BALTIMORE, February, 1877.

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LIST OF ELEMENTS AND ATOMIC WEIGHTS.

Name of Element.	Symbol.	Atomic weight.	Atomic weight, very accurately determined.
Aluminum	Al	27.4	
Antimony	Sb	122	
Arsenic	As	75	
Barium	Ba	137	
Bismuth	Bi	210	
Boron	B	11	
Bromine	Br	80	79.952
Cadmium	Cd	112	
Cæsium	Cs	133	
Calcium	Ca	40	
Carbon	C	12	
Cerium	Ce	92	
Chlorine	Cl	35.5	35.457
Chromium	Cr	52.4	
Cobalt	Co	59	
Columbium	Cb	94	
Copper	Cu	63.4	
Didymium	D	96	
Erbium	E	113.7	
Fluorine	F	19	
Gallium	Ga	—	
Glucinum	Gl	9.4	
Gold	Au	197	
Hydrogen	H	1	
Indium	In	113.7	
Iodine	I	127	126.85
Iridium	Ir	198	
Iron	Fe	56	
Lanthanum	La	92.5	
Lead	Pb	207	
Lithium	Li	7	7.022
Magnesium	Mg	24	
Manganese	Mn	55	
Mercury	Hg	200	
Molybdenum	Mo	95.8	
Nickel	Ni	59	
Nitrogen	N	14	14.044

LIST OF ELEMENTS AND ATOMIC WEIGHTS—*Continued.*

Name of Element	Symbol	Atomic weight.	Atomic weight, very accurately determined.
Osmium	Os	199.2	
Oxygen	O	16	
Palladium	Pd	106.6	
Phosphorus	P	31	
Platinum	Pt	197.4	
Potassium	K	39.1	39.137
Rhodium	Ro	104.4	
Rubidium	Rb	85.4	
Ruthenium	Ru	104.4	
Selenium	Se	79.4	
Silicon	Si	28	
Silver	Ag	108	107.93
Sodium	Na	23	23.043
Strontium	Sr	87.5	
Sulphur	S	32	
Tantalum	Ta	182	
Tellurium	Te	128	
Thallium	Tl	204	
Thorium	Th	231	
Tin	Sn	118	
Titanium	Ti	50	
Tungsten	W	184	
Uranium	U	240	
Vanadium	V	51.3	
Yttrium	Y	61.7	
Zinc	Zn	65	
Zirconium	Zr	89.6	

PRINCIPLES

OF

THEORETICAL CHEMISTRY.

PART FIRST.

GENERAL DISCUSSION OF ATOMS AND MOLECULES.

I.

ATOMIC THEORY—ATOMIC WEIGHTS, ETC.

General Conceptions.—Substances that occur in nature are, for the most part, not simple substances. They can generally be decomposed into kinds of matter that are unlike—some by one means, some by another. Such substances are called compound. In regard to the means required to separate these compounds into their constituents, a marked difference is noticed in different cases. Sometimes only very simple mechanical processes are required to effect the separation. At other times it is found that, after the application of all purely mechanical processes has failed, the compound yields to the influence of some of the so-called physical forces, as heat, light, electricity. This leads to the conclusion that there are at least two varieties of compound substances. Each of these varieties is more or less strongly characterized by external properties. As regards those which can be decomposed by mechanical means alone, it is true that they possess the combined properties of their constituents; and these constituents are usually contained in the compound in their original forms. As regards the second class of compounds, on the other hand, it is just as true that they do not possess the properties of their constituents; and these constituents are contained in the compounds in forms differing entirely from those originally possessed by them.

Chemism.—Substances which are held together by cohesion or adhesion can be separated by mechanical means. But we have here evidence of the existence of some force which holds substances together, and which cannot be overcome by mechanical means. To this force the name *chemical affinity* or *chemism* has been given. The object of the science of chemistry is the study of this force in its relations to matter; or the study of the action of matter upon matter, as far as it is influenced by this force. In regard to the position which chemistry occupies among the sciences, it will be seen that it is primarily a branch of physics, if to the latter science is given its broadest scope. But, further, chemism always gives rise to the formation of new bodies, and the study of these in their relations to each other becomes a legitimate part of the object of chemistry. This allies the science to that branch of study embraced under the head Natural History. Owing to this twofold character, it is customary to treat the subject as forming an independent science, and, for many reasons, this is the most convenient method.

We have thus far recognized the existence of the force, chemism; and also become acquainted with one of the characteristics of its action. The knowledge of the force remained for a long time in this state, as the methods of investigation at first employed could not disclose its most important characteristics. Up to the latter part of the eighteenth century, the *qualitative* method of investigation was of necessity the principal one employed in the study of chemical phenomena; that is to say, the quality of the substances allowed to act upon each other, and the quality of the product or products were noted, but little attention being given to the *amounts* of the substances employed, or of those obtained as products. As the importance of the *quantitative* method became more and more apparent, the means for applying it also gradually made their appearance. The balance, the *sine qua non* of chemistry, was improved, and, finally, in Lavoisier's hands led to tangible results. To its use is to be ascribed the correct explanation of the phenomenon of combustion, a phenomenon which, considered in all the varied forms in which it is presented to us, must be looked upon as the most important of all chemical phenomena. But, though the explanation of combustion was correctly given, no new property of chemism was discovered. A new example of the kind of action which was already known to characterize the force was added to the list; the key was given to a better understanding of the chemical nature of gaseous bodies; the indestructibility of matter became, perhaps, more distinctly evident than it had hitherto been; but the knowledge of chemism as such remained what it had been up to that time. That a definite result was obtained through a consideration of the quantitative relations of an experiment was the fact which, above all others, gave an impulse to the subsequent development of the science.

Investigations of chemical phenomena now took, in general, a different direction; and soon the united work of many hands succeeded in establishing a fundamental principle of the science. The first semblance of a general law governing chemical action made its appearance when it was finally established beyond a doubt that the combination of bodies, under the influence of chemism, always takes place in fixed proportions. This principle, though perhaps tacitly acknowledged by many chemists, was not fully established until the beginning of the present century. In 1803, a strong effort was made by Berthollet, in his work entitled "Statique Chimique," to prove the incorrectness of the principle, but the opposition called forth by this work, particularly from Proust, led to more and more careful examinations of the so-called chemical compounds, and thus to the firm establishment of the principle. Proust also showed that two bodies could combine with each other in more than one proportion, and that for each combination the relative proportions of the constituents were fixed.

Dalton's Investigations.—In the year 1804, Dalton's investigations enabled him to take another advance-step. Another general law governing chemical action was discovered and propounded. This was the *law of multiple proportions.* As this is the foundation of the science, as it is at present, let us follow, somewhat in detail, Dalton's reasoning. Many substances had been analyzed before his time, and the percentages of the constituents had been determined with a tolerable degree of accuracy. He examined first two gases, both of which consist of carbon and hydrogen, viz., olefiant gas and marsh-gas. He analyzed them both, and determined the percentage of the constituents contained in them. These percentages were as follows:—

Olefiant gas, 85.7 per cent. carbon, and 14.3 per cent. hydrogen.
Marsh-gas, 75.0 " " 25.0 " "

On comparing these numbers he found that the ratio of carbon to hydrogen in olefiant gas was as 6 to 1; whereas, in marsh-gas it was 3 to 1, or 6 to 2. The amount of hydrogen combined with a given amount of carbon was exactly twice as great in the one case as in the other.

For the two oxides of carbon, further, the following numbers were obtained:—

Carbon monoxide, 42.86 p. c. carbon, and 57.14 p. c. oxygen.
Carbon dioxide, 27.27 " 72.73 "

But 42.86 : 57.14 : : 6 : 8, and 27.27 : 72.73 : : 6 : 16. The amount of oxygen combined with a given amount of carbon in carbon dioxide was exactly twice as great as the amount of oxygen combined with the same amount of carbon in carbon monoxide. He saw again that, in olefiant gas, one part by weight of hydrogen combined with six parts by weight of carbon; and that in carbon monoxide eight parts by weight of oxygen combined also with six parts by weight of carbon. Water was now examined. It contains 88.89 per cent. oxygen and 11.11 per cent. hydrogen; and these numbers are to each other as 8 to 1. The numbers which, in the first place, represented the combining proportions of oxygen and hydrogen respectively with carbon, are also found to represent, in the second place, the combining proportions of oxygen and hydrogen with each other. All subsequent examinations of other compounds led to similar results, and thus Dalton had discovered the law of multiple proportions. This may be stated as follows:—

If two bodies, A and B, form several compounds with each other, and we consider any fixed amount *of A, then the different amounts of B which combine with this fixed amount of A bear a simple ratio to each other.*

This is a fixed law, and it was generally acknowledged as such by contemporaneous chemists. Thus another characteristic of chemism was clearly pointed out.

Atomic Theory.—But Dalton did not stop with the discovery of the law of multiple proportions; he sought for its explanation. He was thus led to propose the *atomic theory*, as affording the simplest explanation of the facts as observed.

The question as to the ultimate constitution of matter had frequently and from the earliest dates been discussed. Two views were held at different periods and by different thinkers. One of these supposed matter to be indefinitely divisible. The other supposed that there was a limit to the divisibility, and that this limit was reached when the division had been carried down to certain small particles called *atoms*. After the discovery of the law of multiple proportions, however, the atomic theory was further developed, and, in consequence, acquired a more definite form, as the existence of atoms was supposed to have a direct connection with chemical combinations. The results of Dalton's investigations are not fully stated in the law of multiple proportions as above given; another fact was made clear which is also of importance. The complete results may be stated as follows: It was shown that for each element a particular number might be selected; and that this number or a simple multiple of it would represent the proportion by weight in which this element combined with other elements. Dalton explained this by supposing that chemical action takes place between atoms, *i. e.*, between particles that are indivisible and have definite weights. If chemical combination takes place between one atom of one substance and one atom of another substance, or between a simple number of atoms of one substance and a simple number of atoms of another, and these atoms have definite weights, then indeed the explanation of the laws of definite and multiple proportions is given.

Thus the idea of atoms became a much more tangible one than it had been up to that time. Not only were atoms supposed to have definite weights, but a method was given by means of which their relative weights could be determined. The number assigned to an element, representing its combining proportion, would also represent the relative weight of its atom. The fact that the combining proportion of an element was in some cases represented by a multiple of the simplest number was satisfactorily accounted for by supposing that in these cases more than one atom of the element combined with one atom of another element.

Determination of Atomic Weights.—The determination of atomic weights became now the chief, immediate problem of the science of chemistry. Dalton's atomic theory was accepted by many, though not by all. The laws governing chemical combinations could not be doubted, but the explanation could be and was. Nevertheless, the importance of determining for each element the characterizing number, call it atomic weight or combining proportion, was acknowledged by all; and consequently particular attention was given to this field of research during the period directly following Dalton's publication. Let us see how thoroughly the desired object could be accomplished alone by the aid of the principles laid down by Dalton.

At the time of which we are speaking, the methods for chemical analysis were still far from perfect, and hence most of the determinations then made required subsequent corrections which were gradually forthcoming as the analytical methods were improved. This fact, however, has nothing to do with the subject under consideration. The principle alone is involved. The question is to be answered: Can we, on logical grounds, with the principles contained in Dalton's investigations, ever determine the relative weights of the atoms of elements? To decide this question we must first examine more carefully Dalton's method for determining atomic weights. In the following brief discussion the correct numbers, as given by later analyses, are employed, instead of those originally found. This does not interfere with the principle, and does simplify the matter otherwise.

Method for the Determination of Atomic Weights dependent upon Analysis.—As the standard the combining number of hydrogen was first selected, and this made 1. Hydrogen combines with oxygen in the proportion of 1 : 8; and as water was the only known compound of hydrogen and oxygen, the conclusion was drawn that the two elements were united atom to atom, and hence the atomic weight of oxygen was 8. Further, nitrogen is combined with hydrogen in ammonia in the proportion of 1 part by weight of hydrogen to 4⅔ parts by weight of nitrogen. Ammonia was the only compound of nitrogen and hydrogen known; and the same reasoning, as above employed, led to the conclusion that the atomic weight of nitrogen was 4⅔. Considering for a moment these two simple cases, we see that the numbers thus found, as representing the relative weights of the atoms of oxygen and nitrogen, are founded partially upon hypothesis. There is nothing to decide as to the number of atoms of hydrogen or oxygen that are contained in water, nor of nitrogen and hydrogen in ammonia, and, of course, as long as this number is unknown, it is impossible to draw any positive conclusion with reference to the atomic weights of nitrogen and oxygen. Any conclusion thus drawn is dependent upon a thorough knowledge of the compounds of the particular element under consideration. Such a number must finally be selected as is most in accordance with the facts. This selection must remain more or less arbitrary, as may be more clearly and decidedly shown.

Take again the case of oxygen. A second compound of hydrogen and oxygen is now known containing the elements in the proportion 1 : 16. At first sight, the explanation of this may appear simple enough. In this second compound there are two atoms of oxygen combined with one of hydrogen, and thus the proportion is satisfied. But may we not with equal right decide that in water there are two atoms of hydrogen combined with one of oxygen? This would give us for oxygen the atomic weight 16, and, in the second compound, we would have contained one atom of each of the elements.

Further, if we attempt to determine the atomic weight of carbon by Dalton's method, we shall encounter difficulties fully as great, and our final selection among many numbers will be arbitrary. Taking olefiant gas, we have hydrogen combined with carbon in the proportion 1 : 6; in marsh-gas the proportion of the same constituents is 1 : 3 or 2 : 6. If we suppose that in olefiant gas the elements are combined atom with atom, then the atomic weight of carbon would be 6, and consequently in marsh-gas we would have two atoms of hydrogen combined with one atom of carbon. But here again we can just as well suppose that in marsh-gas we have the simplest kind of combination, and this would give us for the atomic weight of carbon 3. Then in olefiant gas two atoms of carbon would be combined with one atom of hydrogen.

Finally, let us take the oxygen compound of carbon. In carbon monoxide, carbon is united with oxygen in the proportion of 6 : 8 or 3 : 4; whereas in carbon dioxide the corresponding proportion is 3 : 8 or 6 : 16. Now let us suppose the atomic weight of oxygen to be equal to 8, then, if carbon monoxide is the simpler of the two compounds, the atomic weight of carbon is 6; and in carbon dioxide there are two atoms of oxygen combined with each atom of carbon. Here, again, it is evident that we can just as well imagine carbon dioxide to be the simpler compound, in which case the atomic weight of carbon would be 3, and in carbon monoxide there would be two atoms of carbon combined with one atom of oxygen. Between these different possibilities it is impossible to draw a logical conclusion with the aid of the knowledge which can be obtained by analysis. The number of similar instances might be increased indefinitely; the inadequacy of the method could be made more strikingly clear by examples of a more complicated kind, but the cases mentioned are sufficient for our purpose; we are obliged to look for other methods for the determination of atomic weights if we would free the numbers from arbitrariness.

Equivalents.—This necessity was recognized first and most clearly by Wollaston in 1814. As no method presented itself to him which would furnish a firm foundation for the determination of atomic weights, he proposed to abandon the idea of atomic weights entirely, and to substitute for it that of the *equivalent*, thus, as he supposed, getting rid of all hypotheses and obtaining numbers that would be the simple expressions of proved facts. The equivalent of an element was to him that quantity of the element that possessed the same chemical value as a given quantity of another element, that quantity of an element that could play the same role as a given quantity of another element. According to the conditions of this definition, it is plain that, in order to know what portions of two elements are equivalent, we must be able to compare the two. Hence, primarily, only of such elements as can be compared with each other, of such as possess a certain degree of similarity, can the equivalent quantities be determined. As this direct comparison is not always, nor, indeed, in the majority of cases, possible, recourse must be had to indirect comparison.

To illustrate this let us take an example. Hydrogen and chlorine combine with each other in the proportion of 1 part by weight of hydrogen to 35.5 parts by weight of chlorine, and from this fact we draw the conclusion that 35.5 parts of chlorine are equivalent to 1 part of hydrogen. We find in the same way that 8 parts of oxygen, 80 of bromine, 16 of sulphur are all equivalent to 1 part of hydrogen. Knowing that 35.5 represents the equivalent of chlorine, we determine the quantities of sodium and silver that are respectively equivalent to this quantity of chlorine. We find for sodium 23 and for silver 108. These quantities of silver and sodium are further found to be equivalent to 8 parts of oxygen, 80 parts of bromine, and 16 parts of sulphur, and hence we conclude that they are also equivalent to 1 part of hydrogen. Thus the equivalents of sodium and silver have been determined by the method of indirect comparison. Sodium and silver do not combine with hydrogen, yet the equivalent numbers found are intended to express the proportions in which they would combine with hydrogen, provided such combination were possible. We are amply justified in this in most simple cases, but nevertheless it must be distinctly borne in mind that such numbers as are determined by indirect comparison with the standard, whatever this may be, are not in the strictest sense expressions of proved facts; the last step in the determinations, however justified we may be in taking it, requires, nevertheless, the aid of hypothesis.

But if *the difficulty* thus referred to were the only one to be met with in the determination of equivalent numbers, such determinations would have nearly the full value claimed for them by Wollaston. This, however, is not the case. As soon as we consider any but the simplest forms of compounds, we are left in fully as much doubt in regard to the equivalent numbers as we were in regard to atomic weights. If it be required to determine the quantity of carbon that is equivalent to 1 part of hydrogen, the compounds of the two elements must be examined. But there are a great many compounds of these two elements. Taking but two, olefiant gas and marsh-gas, we find that in the former (see *ante*, p. 16) 1 part of hydrogen is combined with (equivalent to) 6 parts of carbon; whereas, in the latter, 1 part of hydrogen is combined with (equivalent to) 3 parts of carbon. What shall here decide which is the correct number? It is evident from such instances as this that the idea of equivalent is fully as uncertain as that of the atom was at the time we are considering. That an element could be equivalent to two entirely different quantities was in itself somewhat paradoxical, if the original definition of equivalent was retained. These difficulties seem not to have been apparent to Wollaston. He continued his determinations of equivalents, and during this time a fusion of the ideas of equivalent and atomic weight took place unconsciously. As neither of these ideas was then definite, as to each of a number of elements a number of atomic weights could be assigned, and almost as many equivalents, the succeeding period in the history of chemistry presents a disagreeably confused condition, until it became felt on all sides that some new idea or ideas must be introduced, if a fair foundation for the science was to be reached.

Determinations by Berzelius.—Before the necessary new ideas were introduced, the methods at hand were employed to the full extent. All known compounds of any given element were compared with each other, and a number finally selected, that would best satisfy the facts, to represent the equivalent of the element, or its atomic weight, as it was called by others. Berzelius attacked the subject most successfully. He laid down rules, by the aid of which the number of atoms of an element contained in a compound could be determined, and hence also its atomic weight. Then, by more careful analyses than had been previously made, the atomic weights or equivalents of all the elements were determined. A large number of these determinations depended for their correctness upon chemical rules, similar to the following, given by Berzelius:—

> *If an element forms several oxides, and the quantities of oxygen contained in them, as compared with a fixed quantity of the element, bear the proportion* 1 : 2, *then it is to be concluded that the first compound consists of one atom of the element and one atom of oxygen; the second, of one atom of the element and two atoms of oxygen* (*or two atoms of the element and four atoms of oxygen*). *If the proportion is* 2 : 3, *then the first compound consists of one atom of the element and two atoms of oxygen; the second, of one atom of the element and three atoms of oxygen, etc.*

This rule covers those cases in which it is required to determine the atomic weight of an element by a consideration of its oxides. Other rules were given in which sulphur compounds, etc., were made the basis of calculation.

It will be observed that, although in these rules the oxygen and sulphur are taken as the elements, the number of whose atoms varies, the other elements might theoretically be considered in the same way, and the atomic weights obtained would then be entirely different. An example will make this clear: Mercury combines with oxygen in two proportions. In the first compound, 8 parts of oxygen are combined with 200 parts of mercury; in the second, 16 parts of oxygen are combined with 200 parts of mercury. Adopting the rule above laid down, we would conclude that, in the first compound, 1 atom of mercury is combined with 1 atom of oxygen; and in the second, 1 atom of mercury with 2 atoms of oxygen. If, then, 8 is the atomic weight of oxygen, 200 is the atomic weight of mercury. But if, on the other hand, we consider the quantity of oxygen as remaining fixed, and that of the mercury as varying, then we would have in the first compound, 8 parts of oxygen combined with 200 parts of mercury, and in the second, 8 parts of oxygen combined with *100* parts of mercury; and, by a similar process of reasoning, we might draw the conclusion that the first compound contains 2 atoms of mercury to 1 atom of oxygen, and the second, 1 atom of mercury to 1 atom of oxygen; and thus we would obtain 100 as the atomic weight of mercury instead of 200, as found above. Berzelius had made certain observations on chemical bodies upon which he based his rules, but, as we shall see, these observations were not sufficient.

Another difficulty presented itself in the case of those elements that only combined in one proportion with oxygen. What should decide in regard to the number of atoms of oxygen contained in a compound of such an element? Here speculation was the only aid, and it often led to false results.

The Principle of Substitution employed in the Determination of Atomic Weights.—The researches of Berzelius added a vast amount to the knowledge of the combining weights of the elements, and it must be acknowledged that the determinations made by him rested upon a somewhat firmer basis than the determinations made previously. He made the fullest and most logical use of purely chemical means that could be made at the time. Subsequently, however, a new fact was discovered in connection with chemical compounds which proved of great value in simplifying the consideration of chemical phenomena, and also aided materially in the solution of the problem of the determination of atomic weights. This is *substitution*. The subject will be considered more fully in the last section; here a brief explanation will suffice for the purpose of exhibiting its connection with the problem with which we are at present dealing. It has been found that certain elements have the power of entering into compound bodies, driving out some of the constituents, and taking the place thus left vacant. For instance, water contains 2 atoms of hydrogen and one of oxygen; if we allow potassium to act upon water, a portion of the hydrogen is given off, and a new compound containing both potassium and hydrogen, in addition to the oxygen, is the result. If now potassium be further allowed to act upon this new compound, the hydrogen contained in it will be driven out, and its place will be taken by potassium. Thus we obtain from water, by replacing its hydrogen by potassium, a compound containing 2 atoms of potassium and 1 atom of oxygen. This kind of action is called *substitution.*

To show how, by taking into account the transformations included under this head, we may draw conclusions of importance with reference to atomic weights, one simple example may suffice: We have seen that the chief difficulty in determining atomic weights or equivalents by chemical means consists in the lack of data for estimating the number of atoms of an element contained in any given compound. Considering marsh-gas, we find that in it 1 part of hydrogen is combined with 3 parts of carbon, and, as above stated, we might conclude from this fact that the atomic weight of carbon is 3. If, however, we can by any means prove that there are more than one atom of hydrogen contained in the gas, the conclusion would require modification. By means of the process of substitution, this can be proved. By allowing chlorine to act upon marsh-gas under proper conditions, a portion of the hydrogen will be replaced, and a compound containing carbon, hydrogen, and chlorine will result. This new compound treated with chlorine again gives up a portion of its hydrogen, and takes up chlorine in its place. This operation may be repeated four times, and thus finally a compound is obtained which contains only carbon and chlorine. Each time the same amount of hydrogen is given up, and is replaced by an equivalent amount of chlorine. Thus it is plain that the hydrogen originally contained in marsh-gas is divisible into four parts, and we are obliged to accept the conclusion that there are *at least* four atoms of hydrogen contained in marsh-gas—a conclusion which we could not possibly reach by the aid of the means heretofore considered. If now we take that amount of carbon which is in combination with four atoms of hydrogen as representing one atom (and, by a consideration of the whole list of carbon compounds, we are justified in this step), then the atomic weight of carbon is 12. The method thus briefly illustrated is capable of application to a considerable extent, but not to such an extent as to render it a general method for the determination of atomic weights.

Consideration of Chemical Decompositions for the purpose of determining Atomic Weights.—One more method of reasoning must be referred to as having been employed, either for the purpose of furnishing proofs of the correctness of atomic weights determined by other means, or for the direct determination of these weights. An example will best make this matter clear. We wish to know, for instance, how many atoms of hydrogen are combined with nitrogen in ammonia; or, having by the preceding method concluded that this number is 3, we wish to verify the conclusion by other observations. By treating nitric acid (which we will suppose to contain one atom of hydrogen to every atom of nitrogen) with hydrogen, we obtain ammonia. Now, if we consider the amount of hydrogen that in nitric acid was in combination with the nitrogen, we find that, in the resulting ammonia, three times as much hydrogen is combined with the same amount of nitrogen. Further, ammonia combines directly with a number of compounds, and, if we examine the amount of hydrogen contained in this ammonia, we find that it must necessarily be represented with three or some multiple of three atoms of hydrogen. Thus, if we study the various cases in which ammonia is either formed, or destroyed, or enters into combination, we find always that the quantity of ammonia thus playing a part must contain three or some multiple of three atoms of hydrogen; and hence we are again led to the conclusion that, in ammonia at least, three atoms of hydrogen are combined with every atom of nitrogen.

The methods we have thus briefly described comprise all we have at our command for the determination of atomic weights dependent upon purely chemical processes. Consider these methods as we may, we must see that they are inadequate to the accomplishment of their object. The determinations may indeed be made, but at last there must always remain a doubt concerning the result. If then we can approach the subject from an entirely different direction, we shall succeed in reducing this doubt to a minimum, if we find that the results at first obtained assert themselves as correct in the second instance. Before passing, however, to a consideration of new methods for making these determinations, it will be well to apply the knowledge we have gained in fixing more definitely than has yet been done the ideas of elements and compounds.

Elements.—The theoretical idea of an element has already been stated. An element, strictly speaking, is a substance that cannot by any possible means be decomposed into kinds of matter that are unlike. This definition presupposes a knowledge of all possible means for decomposing bodies. Until we are positive that we are acquainted with all these means, we cannot be positive in regard to the existence of a single element. But it is plain that to assert the possession of this amount of knowledge would be in the highest degree presumptuous. We can then never assert positively that any given substance is an element; we can only say that, the means at our command being insufficient to bring about the decomposition of a given body, we consider this substance an element until such time shall arrive when, new means being given, it shall be shown to be compound. Numerous instances of the change of opinion concerning the elementary character of different substances might be adduced, prominent among which would be the alkaline metals, the oxides of which were for a time looked upon as elements; chlorine, which was looked upon as a compound body until it had been satisfactorily shown that we were not in possession of the means for decomposing it, etc. etc. Thus the number of elements, as stated at any given time, is entirely dependent upon the state of chemical analysis at that time, and is never an expression of an absolute fact. At present, the number of elements known is 64. In other words, we can recognize the existence of 64 different kinds of matter.

If we consider the atoms which make up an elementary substance, we see that they must necessarily be of the same kind, how far soever, we consider the subdivision of the substance as taking place before the atom is reached. Accepting then the existence of atoms, an element may be defined as a substance made up of atoms of the same kind; and we shall see that the definition of an atom, which will be given further on, makes this definition of an element a strict one in every respect.

Compounds. — It has been stated that observation shows us the existence of at least two varieties of compound bodies. To only one of these, however, is the name *compound* strictly applied, and then the name signifies a *chemical compound*. To the other class various names are applied, according to the nature of the substance, such, for instance, as *mechanical mixture*, *solution*, *alloy*, etc. At one time it was thought that no strict line of division could be drawn between these two classes. The same ultimate causes were supposed to give rise to the formation of both; and the constituents of both were supposed to be held together by the same agent. It may be shown that there is a marked difference between them, sufficient to enable us to say, in most cases, with which we have to deal.

Firstly, if we examine chemical compounds, we find that one of their most prominent characteristics is the possession of properties which differ entirely from those of their constituents. Hydrogen, an inflammable gas, and oxygen, a gas and energetic supporter of combustion, combine to form a liquid, water, which is not inflammable and does not support combustion. Hydrochloric acid, a gas that turns vegetable blues red, and ammonia, a gas that turns vegetable reds blue, unite to form sal-ammoniac—a solid that is without influence upon vegetable colors. Chlorine, a gas, and mercury, a liquid, give a solid with none of the properties of either. The number of these examples might be increased indefinitely, and in each case a similar result would be reached.

Secondly, it will be found that no purely mechanical means will suffice to separate the constituents of a chemical compound from each other; but for this purpose one of the so-called physical forces, as heat, light, electricity, chemism, is necessary.

Thirdly, the most important characteristic of chemical compounds is to be found in the proportion by weight in which the constituents are bound together. As regards any compound of two elements, it is a fact that the constituents are present in fixed proportions by weight. If we bring these elements together without reference to their quantities, and the proper conditions be brought about to induce combination, it is found that a definite quantity of one combines with a definite quantity of the other; and, if the quantity of either present is in excess of the fixed quantity necessary for the formation of the compound, this excess will remain in its original form after combination has taken place. We can only vary the proportions to a very limited extent, and then not gradually, but according to a fixed rule. This is the circumstance which above all others enables us to assert positively that a given body is or is not a chemical compound.

Mechanical Mixtures.—To compare the second class of compounds with chemical compounds proper, let us first take the so-called mechanical mixtures. If we bring oxygen and nitrogen together, a homogeneous mixture of the two is formed, and this possesses the properties of both oxygen and nitrogen; such a mixture, for instance, is the atmosphere of the earth. Gases mix in this way by virtue of their inherent tendency to expand indefinitely and completely fill the space offered to them. It is hence unnecessary to suppose that any special force acts in this gas to hold the constituents together. Many solids may be mixed in various ways, but no matter how finely we may divide them, nor how intimately we may mix them, provided chemical combination does not take place, we can again separate the constituents of the mixture by mechanical means; and the mixture possesses all the original properties of its constituents. In both these cases, further, the most varied quantities of the substances may be employed, and, under the same conditions, the mixtures will be formed just as readily with one proportion as with another.

Solutions and Alloys.—On the other hand, those compounds which are known under the names of solutions and alloys are more closely allied to chemical compounds. We may have gases, liquids, or solids in the state of solution, that is, in combination with some liquid body, and to all appearance themselves in the liquid form. The external properties of one of the constituents are no longer recognizable, and they are, indeed, in part lost. A gas loses its ordinary elasticity when dissolved in a liquid. A solid loses the cohesion which before held its particles together. Two liquids combined in this way lose some of their original properties, and receive new ones that represent a mean between the lost ones. In all these instances some force must be imagined as acting between the particles of the dissolved bodies and the particles of the solvents, which is greater in its effect than the cohesion that originally held together the particles of the solid or liquid, or the repulsion that was exerted between the particles of the gas. Further, we have the case of alloys or compounds of two or more metals. These alloys present all the appearance of perfectly homogeneous bodies, but nevertheless possess most of the properties of the constituents. Here, too, some force must be considered as acting between the unlike particles which differs from the ordinary force of cohesion.

On examining the above-mentioned cases more carefully, we find that there is, in almost all cases, a limit to the action of the force. Substances that are soluble in water are not usually soluble to an unlimited extent; on the contrary, for any given temperature, the proportion of the substance that can be dissolved is fixed. But, between this fixed amount and the smallest possible quantity of the substance, all proportions are equally well dissolved. Some liquids mix with each other in all proportions, a perfectly homogeneous liquid being the result. Others dissolve each other to only a limited extent, the limits being, as in the case of solids and liquids, fixed for any given temperature.

Whatever the force may be that is supposed to be the essential agent in the formation of these compounds in variable proportions, it is certain that the law or laws of its action have not been discovered up to the present. Some have looked upon it as identical with chemism, yet it appears that very distinct differences between the two can be pointed out.

The first feature of these compounds that indicates a radical difference in the two forces is the retaining of the chief original properties of the constituents. If we dissolve sodium chloride in water, we can obtain all the important effects from the solution that we could from the solid substance, and added to these we would then further obtain the effects of the water. And the same holds good for all solutions; they can produce the effects of the substances dissolved and of the solvent combined.

As we have seen, this is not true of chemical compounds proper.

Again, and most especially is the difference marked, if we consider the proportions by weight in which the substances combine in the two cases. Whereas, whenever chemical compounds are formed, the constituents combine in fixed proportions,—in the case of mixtures, solutions, alloys, the constituents may combine in all possible proportions up to a certain fixed limit.

Whether it would be expedient then to consider chemism and the force that is the cause of the formation of solutions, etc., as identical, but differing in degree, is a question that cannot be here discussed. Certain it is, from the above remarks, that there exists sufficient difference between them to warrant us for the present in restricting the use of the name chemism to the designation of that force which is the essential cause of the formation of chemical compounds. In this sense it will be used in the following pages. The atomic theory accounts for the fact that bodies combine in definite proportions by supposing them to combine atom to atom, and these atoms to possess definite weights. According to this, chemism, in its restricted sense, is the force which is exerted between atoms. It will be shown that these atoms may be either like or unlike. If they are like, the resulting body is an element; if they are unlike, the resulting body is a chemical compound.

It is plain, from the foregoing, that chemical compounds and elements are the only substances the study of which can lead to definite conclusions concerning the action of chemism, and hence we must confine ourselves to these in our subsequent study of this force. And first, we must return to that fundamental problem of chemistry —the determination of atomic weights. It having been shown that results reached by the methods already given must necessarily be uncertain, we now proceed to attack the subject from a wholly new side.

II.

EXAMINATION OF GASEOUS ELEMENTS AND COMPOUNDS.

As bodies present themselves to us in three different states of aggregation, the solid, liquid, and gaseous, so our methods of investigation of bodies must take different directions. The gases possess certain properties that are not possessed by solids and liquids, and in solids and liquids we detect certain general properties that we cannot detect in gases. The study of bodies in the form of gas or vapor has led to very important results of lasting influence upon the science, and to these let us direct our attention.

Investigations of Gay Lussac.—In the year 1808, Gay Lussac and Humboldt discovered the fact that when hydrogen and oxygen combined to form water, the combination takes place between 2 volumes of hydrogen and 1 volume of oxygen. The simplicity of this relation induced Gay Lussac to take up the study of other gaseous bodies, with the view of determining whether similar relations existed between the volumes of other combining gases. His researches permitted him soon after to deduce the following law of combination by volumes:—

> *When two or more gaseous constituents combine to form a gaseous compound, the volumes* of the individual constituents as well as their sum bear a simple relation to the value of the compound.*

Thus, when hydrogen and chlorine unite to form hydrochloric acid, it was found that 1 volume of hydrogen and 1 volume of chlorine formed 2 volumes of hydrochloric acid gas. Two volumes of hydrogen and 1 volume of oxygen gave 2 volumes of water-vapor; 2 volumes of nitrogen and 1 volume of oxygen gave 2 volumes of nitrous oxide. Further, 3 volumes of hydrogen and 1 volume of nitrogen gave 2 volumes of ammonia, etc. etc.

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* In all cases where the volumes of different gases are compared, the gases are, of course, supposed to be under the same conditions of pressure and temperature.

On comparing this result with that already obtained by Dalton, and making use of the atomic theory, according to which combination between elements takes place between their atoms, we see that some simple relation exists between the volumes of gases and the relative number of atoms contained in these volumes. This we may express in general terms as follows:—

The number of atoms contained in a given volume of a gaseous body forms a simple ratio with the number of atoms contained in the same volume of other gaseous bodies.

As will be readily seen, this gives no foundation for the determination of atomic weights, inasmuch as we have no means of fixing the value of the "simple ratio," and without this we cannot determine the relative number of atoms contained in a given volume of gas. We know that 2 volumes of hydrogen combine with 1 volume of oxygen, and we know that 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen. Further, the atomic theory tells us that a certain number of atoms of hydrogen of fixed weight combine with a certain number of atoms of oxygen of fixed weight, and that these numbers bear a simple relation to each other; hence the relation between the number of atoms of hydrogen in the 2 volumes, and the number of atoms of oxygen in the 1 volume, must be a simple one, but the facts do not furnish us with sufficient data to enable us to state what this relation is; without further aid either from new facts or speculations, we cannot say what the atomic weights of these elements are.

Avogadro's Speculations.—The numbers expressing the specific gravities of gases or vapors are those numbers which express the relative weights of like volumes of these gases or vapors. Hence it is but restating, in another form, the principle above laid down to say that the specific gravities of gaseous bodies bear a simple relation to the atomic weights of these bodies. The force of this statement will be readily recognized on comparing the specific gravities of some gases with the atomic weights of the same bodies determined by chemical means. The atomic weights as determined by chemical means, however, differed from each other according to the method employed in this determination; but the difference being that between one number and some multiple of that number, it is immaterial which of these numbers we employ for the purposes of the comparison. Let us then take the first of those determined. The following table hardly needs explanation. The numbers in the second column (d) represent the specific gravities of the elements in the form of gas or vapor; the fourth column contains the ratios between the atomic weights (A) and $d = \frac{A}{d}$.

Element.	d.	A.	$\frac{A}{d}$.
Hydrogen	0.0692	1	14.45
Chlorine	2.440	35.5	14.55
Bromine	5.54	80	14.44
Iodine	8.716	127	14.57
Oxygen	1.10563	8	7.24
Sulphur	2.23	16	7.17
Selenium	5.68	39.7	6.99
Tellurium	9.08	64	7.05
Nitrogen	0.9713	14	14.41
Phosphorus	4.50	31	6.89
Arsenic	10.6	75	7.08
Mercury	7.03	100	14.22
Cadmium	3.94	56	14.21

We see thus that the relation between the specific gravity and the atomic weight of seven of these thirteen elements is the same, being expressed by a number varying but little from 14.4. In the six remaining elements of the list also the relation is virtually the same, about 7.1. And, in the latter case, the ratio is expressed by a number half as great as the first.

A consideration of these relations led Avogadro,* in 1811, to propose an hypothesis which, if it could be well founded, would prove of the greatest service in simplifying the problem of determining the atomic weights—at least of gaseous bodies. It will be seen that, if in the above schedule the atomic weights of oxygen, sulphur, selenium, tellurium, phosphorus, and arsenic be doubled, the ratio $\frac{A}{d}$ for all the elements in the list will be the same constant number, viz., about 14.4. But the atomic weights above given have been determined purely empirically, and we are as much justified in considering these numbers doubled the true atomic weights, as we are in accepting the ones given. If we make this change, then for the above thirteen elements, the following statement would be true: The atomic weights are to each other as the specific gravities of the vapors. An examination of compound gaseous bodies showed further that a simple relation also existed between their specific gravities and the numbers expressing the sum of the atomic weights of the constituents, these sums being to each other as the specific gravities. Avogadro's hypothesis to account for these relations may be stated in the following words:—

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* In 1814 Ampère proposed a similar hypothesis.

> *All gases or vapors, without exception, contain, in the same volume, the same number of ultimate particles or molecules.*

The molecules were not considered to be identical with the atoms, and it is well here to draw the distinction between the two as clearly as possible. Molecules of compounds, as understood by Avogadro, and as understood at present, are the theoretically smallest particles of these compounds. The molecule of water is the smallest particle of water that can exist as water. As water, however, is composed of two elements, of course the smallest particle of water must necessarily still be divisible into these constituents. The component parts of molecules are called atoms, and these are indivisible. In the case of water, the molecule has the same composition as the mass of the compound, but, as will be shown, this molecule of water consists of two atoms of hydrogen and one atom of oxygen. The atoms are held together by chemism, the molecules by cohesion.

Now there are good reasons, which will be considered below, for believing that, in their internal structure, elementary substances are, in some respects, analogous to compounds, and this belief was made a fundamental condition of Avogadro's hypothesis. According to this, it is impossible by purely mechanical means to subdivide an element so far as to reach its atoms; but if we suppose it divided as far as possible by such means, we reach, as in the case of compounds, the molecule of the element, which is the smallest particle of the element that can exist and play the part of the element. This molecule, however, usually consists of atoms which are held together by chemism, and can hence only be separated by some means, other than mechanical, that are known to have the power of overcoming the force.

From these considerations we are enabled to give definitions of the terms *atom* and *molecule*:—

> *A molecule is the smallest particle of a compound or element that is capable of existence in a free state. A breaking up of the molecule necessitates the destruction of the properties of the compound, and almost always of those of the element.*
>
> *Atoms are the indivisible constituents of molecules. They are the smallest particles of elements that can take part in chemical reactions, and are, for the greater part, incapable of existence in the free state, but are always found in combination with other atoms, either of the same kind or of different kinds.*

And now the justice of the definitions of elements and compounds given above (see pp. 27, 28) will be recognized, viz., an element is a substance made up of atoms of the same kind; a compound is a substance made up of atoms of unlike kind.

Recognizing thus fully the distinction between atoms and molecules, we are prepared to further follow the reasoning of Avogadro.

The experiments of Gay Lussac had already proved that, under the influence of heat, all gases expand in the same proportion for the same increase of temperature, and diminished in volume to the same extent for the same decrease of temperature. Further, Mariotte, in France, and Boyle, in England, had shown that all gases conducted themselves in the same way under the influence of increased or decreased pressure; that for the same increase or decrease of pressure the consequent decrease or increase of volume was for the same volume of all gases the same. These facts considered independently would lead to a suspicion that all gases possess a similar internal structure, and the simplest hypothesis to account for this is just the hypothesis of Avogadro—that the same volumes of all gaseous bodies contain the same number of molecules. This subject has been considered exhaustively from a purely physical standpoint. The principles of the mechanical theory of gases being accepted, it was shown that the hypothesis of Avogadro would logically follow; and then, by a purely mathematical process of reasoning, it was shown that the hypothesis was an absolute necessity. A discussion of the subject in the direction indicated cannot here be taken up. For those who desire to follow the discussion, and to become acquainted with the methods that have led to the result mentioned, the following references will be of service: Krönig, Poggendorff's Annalen, 99, 316; Clausius, Pogg. Ann., 100, 360; Naumann, Annalen der Chemie u. Pharmacie, 1870, Suppl. Band 7, 340; Pfaundler, Pogg. Ann., 144, 428; Maxwell, Phil. Mag., 1860, [4] 19, 19; Phil. Trans., 1867, 1; Phil. Mag., 1868, [4] 35, 185; Thomsen, Berichte der deutsch. chem. Gesellschaft zu Berlin, 1870, 829; Lothar Meyer, *ibid.*, 1870, 864; Thomsen, *ibid.*, 1870, 954; Lothar Meyer, *ibid.*, 1871, 28; Mees, *ibid.*, 1871, 272.

As a grand result of the investigations that have been made on the internal structure of gases, it may be stated that Avogadro's hypothesis has throughout asserted its correctness, and it has at last become of fundamental importance in the science of chemistry. It is at present almost universally accepted by chemists, some, indeed, going so far as to speak of it as a *law*.

Determination of Molecular Weights.—What, then, do we gain by accepting the hypothesis? It is plain that if equal volumes of all gases contain the same number of molecules, we have a means given us at once for ascertaining the relative weights of these molecules. We have merely to determine the relative weights of equal volumes of the gases, and the numbers obtained will bear the same relations to each other as the molecular weights. Then accepting the weight of some molecule as a standard, and expressing the weights of the others in terms of this standard, the molecular weights are determined. If we call the molecular weight of hydrogen 2, for instance, and find the relation between this number and the number expressing the specific gravity of hydrogen, then we have also found the number expressing the relation between the molecular weights and specific gravities of all gases and vapors, without exception. The specific gravity of hydrogen as compared with air is 0.06926, the ratio $\frac{2}{0.06926} = 28.88$; hence, the specific gravity multiplied by 28.88 gives the molecular weight. If $d =$ specific gravity, $M =$ molecular weight, then the following formula will express the relation:—

$$M = d \times 28.88.$$

As the molecule of a body consists of atoms, so the molecular weight must be the sum of the weights of those atoms. In the case of an element, the atoms being of the same kind, the molecular weight must be a multiple of the atomic weight. Now we have already seen that for every element we can, by chemical analysis, determine some number that must represent either the atomic weight itself or a multiple of this weight. Hence, we have it in our power to determine by chemical analysis a multiple of the molecular weight of an element or a compound. This determination can be made with greater accuracy than that of the specific gravity of a gas or vapor, and it must be employed as a control for the determination of molecular weights by Avogadro's rule. If we take water, for instance, we find by means of analysis that its molecular weight is either 9 or some simple multiple of 9. The specific gravity of water-vapor is 0.623, which multiplied by 28.88 gives 17.99 as the molecular weight. Hence, we conclude that 18 is the true molecular weight of water. The coincidence of the numbers determined according to the two methods will be seen in the case of a few elements and compounds in the following table. The numbers under M are those found by the analytical method, that one of a series of multiples being selected that agrees most nearly with the number found according to the rule $M = 28.88 \times d$.

Name.	Specific gr. = d.	$28.88 \times d$	M.
Hydrogen	0.06926	2	2
Nitrogen	0.9713	28.05	28
Oxygen	1.10563	31.93	32
Sulphur	2.23	64.4	64
Chlorine	2.45	70.75	71
Cadmium	3.94	113.78	112
Phosphorus	4.35	125.62	124
Bromine	5.54	159.99	160
Selenium	5.68	164.03	158.8
Mercury	6.98	201.58	200
Water	0.623	17.99	18
Hydrochloric acid	1.247	36.11	36.5
Sulphur dioxide	2.247	64.89	64
Ammonia	0.597	17.24	17
Phosphorus trichloride	4.88	140.93	137.5
Arsenic trichloride	6.30	181.94	181.5
Boron chloride	3.942	113.84	117.5
Marsh-gas	0.557	16.08	16
Methyl chloride	1.736	50.13	50.5
Chloroform	4.20	121.29	119.5
Tin chloride	9.20	265.69	260
Silicon chloride	5.94	171.55	170
Zinc-methyl	3.29	95.02	95.2
Aluminium chloride	9.35	270.03	267
Iron trichloride	11.39	328.94	325

Number of Atoms in the Molecules of Elements.—Although we are thus enabled by a simple process to determine the molecular weights of some of the elements, an important part of the real problem—the determination of the atomic weights—remains yet to be solved. If we could know in each case how many atoms are contained in a molecule, our difficulties would be at an end, but this we plainly do not know without the introduction of considerations of a different kind from those with which we have had to deal as yet. Avogadro reasoned as follows, with reference to some of the simple chemical compounds: Given hydrochloric acid, it is required to know how many atoms are contained in a molecule of hydrogen and in a molecule of chlorine. If in a certain volume of hydrogen there are contained say 100 molecules, then in the same volume of chlorine there is contained the same number of molecules. Now it is known that 1 volume of hydrogen combines with 1 volume of chlorine. Two volumes of hydrochloric acid gas are formed, and, according to the hypothesis, these two volumes in the case under consideration contain 200 molecules. But each molecule of hydrochloric acid must contain at least one atom of hydrogen and one atom of chlorine; hence, in 100 molecules of hydrogen and 100 molecules of chlorine there must be contained at least 200 atoms of chlorine and 200 atoms of hydrogen, or a molecule of either hydrogen or chlorine must contain at least two atoms of the corresponding element. Further, as no simpler compound than hydrochloric acid of hydrogen nor of chlorine is known, any conclusions which we may draw from a consideration of this compound must be valid for all compounds of these elements. The supposition that two atoms form the molecule of hydrogen and of chlorine satisfies all the facts known to us, and we hence rest with this supposition. As we take the atomic weight of hydrogen as the unit of these weights, its molecular weight will then necessarily be 2, on this basis; and for this reason the number 2 was taken in the above table as the standard of comparison for other molecular weights. It must, however, be distinctly borne in mind that no proof is here given of the absolute number of atoms contained in the molecules of hydrogen and chlorine. We can only say that *at least* 2 atoms must be present in each of the molecules. There may be a much greater number, but the data permit no speculations beyond this number 2.

For all similar cases a similar process of reasoning may be employed, and with the same results. Whenever 1 volume of an elementary gas or vapor combines with 1 volume of another elementary gas or vapor to form 2 volumes of a compound gas or vapor, we are justified in concluding that each molecule of these elements contains two atoms. The elements that come under this head are hydrogen, chlorine, bromine, and iodine.

If we pass to oxygen, we find a material difference in the method of combination. Here 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of water-vapor. Let us reason as above. If in 1 volume of oxygen there are contained 100 molecules, then in 2 volumes of hydrogen there are 200 molecules. These

300 molecules combine to form 200 molecules of the compound. Now, in the molecule of water, there must be contained at least one atom of oxygen and one atom of hydrogen; hence, there must be at least 200 atoms of oxygen and 200 atoms of hydrogen. But we know that in the original 200 molecules of hydrogen there were contained 400 atoms; hence, in each molecule of water, there must be 2 atoms of hydrogen. Water is the simplest compound of oxygen known to us (*i. e.*, it contains the smallest quantity of oxygen in the molecule), and on this account we suppose the molecule of water to contain 1 atom of oxygen. If, then, each water molecule contains 2 atoms of hydrogen and 1 atom of oxygen, in the 200 molecules of water there are 200 atoms of oxygen and 400 atoms of hydrogen, and these are obtained from 100 molecules of oxygen and 200 molecules of hydrogen. Therefore, each molecule of oxygen, as well as each molecule of hydrogen contains 2 atoms. For sulphur the same is true, and is proved in a similar manner.

Another method of reasoning, starting from entirely different facts, also led Favre and Silbermann to suggest that the molecule of oxygen consists of two atoms. They proved that carbon, when burned in protoxide of nitrogen, evolves more heat than when burned in oxygen. The most natural interpretation of this fact consists in admitting that, in each experiment, a chemical combination is destroyed whilst another is formed; and that the amount of heat actually evolved is the difference between the amount of heat disengaged by the union of carbon with oxygen and the amount of heat absorbed by the decomposition of the oxide of oxygen in the first instance, and of oxide of nitrogen in the second. And, if the thermic effect is less with oxygen than with protoxide of nitrogen, that is due to the circumstance that oxide of oxygen (the molecule of oxygen $O=O$) absorbs more heat in decomposing than does the molecule of protoxide of nitrogen.

One volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia. Hence in the molecule of ammonia there are 3 atoms of hydrogen, and, ammonia being the simplest compound of nitrogen, we suppose that these 3 atoms of hydrogen are combined with 1 atom of nitrogen. As each molecule of ammonia contains one atom of nitrogen, and as, further, there are formed twice as many molecules of ammonia as there were molecules of nitrogen originally, it follows that the molecule of nitrogen contains at least 2 atoms.

By this means we are enabled to determine the atomic weight of the elements mentioned, for, if in their molecules 2 atoms are contained, we have only to divide the molecular weight—found by Avogadro's rule, and corrected by analytical methods—by two. But, accepting the atomic weights of hydrogen, chlorine, bromine, and iodine as known, we are enabled by another process to determine the atomic weights of such elements as combine with these to form gaseous compounds.

Take again water. We find by a comparison of the compounds of oxygen that the molecule of water, as stated above, contains the smallest quantity of this element; and hence we suppose this quantity to represent 1 atom. We first find the molecular weight from the specific gravity of the vapor. This is 18. We analyze the compound, and find that it contains 88.89 per cent. oxygen and 11.11 per cent. hydrogen, or 8 parts of oxygen to 1 part of hydrogen. This being the relative proportion of the two elements in the compound, in 18 parts by weight, which represent the molecule, there are contained 16 parts of oxygen and 2 parts of hydrogen. The atomic weight of oxygen is hence 16, and in water one atom of oxygen is combined with 2 atoms of hydrogen. In the case of nitrogen, the application of the same principle must also lead to the same number previously found, viz., 14. We come to the conclusion that the molecule contains one atom of nitrogen. The molecular weight of ammonia we find to be 17. The analysis shows us that the elements are combined in the proportion of 14 parts by weight of nitrogen to 3 parts by weight of hydrogen. Hence 14 is the atomic weight of nitrogen, and the molecule of ammonia contains 1 atom of nitrogen with 3 atoms of hydrogen.

Molecules of Elements which contain more or less than two Atoms.—The molecules of the elements considered contain each two atoms. This is, however, not true of the molecules of all elements.

Among those compounds of phosphorus which may be looked upon as containing 1 atom of this element in the molecule is phosphine. The molecular weight of phosphine is 34. The elements are contained in it in the proportion of 31 parts of phosphorus to 3 parts of hydrogen. Hence 31 is the atomic weight of phosphorus. On the other hand, we find the molecular weight of phosphorus itself to be 124, which shows that at least 4 atoms are contained in the molecule. The same is true of arsenic.

For reasons similar to those given above, the molecule of mercuric chloride is supposed to contain one atom of mercury. The molecular weight of this compound is found to be 270.5, and the elements are contained in it in the proportion of 200 parts of mercury to 71 parts of chlorine, which gives 200 as the atomic weight of mercury; and the atom of this element is combined with 2 atoms of chlorine. The molecular weight of mercury is 200; hence in the molecule of mercury there is contained but one atom. The same coincidence of atomic and molecular weight is noticed in connection with cadmium.*

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* An interesting experiment has recently been performed, the results of which also show that the molecule of mercury in all probability consists of a single atom. The quantity of heat contained in a gas is defined as the total energy of its molecules, and this energy consists solely in advancing motion, if the molecule is looked upon as a mere material point. According to this, it is a simple matter to calculate the relation between the specific heat of a gas at constant volume and the specific heat at constant pressure. It was found, however, that, in the case of the gases examined, the theoretical value of this relation was larger than the value actually obtained by observation. If c represents the specific heat at constant volume, and c' the specific heat at constant pressure, then $\frac{c'}{c} = k$ represents the relation above referred to. According to the theory, $k = 1.67$, whereas observation gives $k = 1.405$. In other words, it requires more heat to raise the temperature of a gas, the volume remaining unchanged, than the theory demands. The heat which thus disappears may be transformed into an inter-molecular motion; *i. e.*, the atoms composing the molecule may have a motion relative to some centre of gravity. This motion would not show itself as temperature. If the molecule of the gas consists of one atom, then the theoretical and observed value of k should be identical. The examination of mercury gave for k the value 1.67, which is that above given as the result of calculation. It is thus shown, by a method entirely independent of chemistry, that the molecule of mercury conducts itself like a material point, and this it could only be if it consisted of one atom.

Varying Number of Atoms in the Molecule of one and the same Element.—The specific gravity of the vapor of sulphur was stated in the above table (p. 39) to be 2.23, and this led to the molecular weight 64. Now it has been found that the specific gravity of this vapor varies according to the temperature at which it is determined. The determinations which gave the number 2.23 were made at temperatures above 800° C. (860° and 1040°). Other determinations, however, made below 800° gave different results. At 524° (Dumas) and 508° (Mitscherlich) the specific gravity was found to be 6.62 and 6.90 respectively, or three times as great as at the higher temperatures. These latter determinations would give the molecular weight 192, and, if 32 be the atomic weight of sulphur, then in the molecule of the vapor below 800° there would be contained 6 atoms, whereas above 800° there are contained only 2 atoms in the molecule. Selenium, so similar to sulphur in all other respects, presents similar phenomena, though not in so marked a degree. Here, too, it is noticed that the specific gravity of the vapor decreases with an increase of temperature, or, what, according to Avogadro's hypothesis, is the same thing, the molecular weight decreases with an increase of temperature.

The application of the method thus described for the determination of the molecular weights of elementary bodies is limited, as we can convert only a few of these bodies into the form of vapor. Of many elements, however, we know compounds that are capable of conversion into vapor or are themselves gaseous; and, as we can determine the molecular weights of these compounds, we are in many cases thus enabled to determine the atomic weights. The following table* contains a number of such compounds, together with the densities (d); the products of the densities into the constant 28.88 ($d \times 28.88$); the molecular weights as found by analytical methods (M); and, finally, the relative quantities of the constituents of the compounds contained in the molecules as determined by analysis:—

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* "Die modernen Theorien der Chemie," Lothar Meyer.

	d.	*d*×28.88	*M.*	Constituents.
Hydrochloric acid	1.247	36	36.5	1 part hydrogen, 35.5 parts chlorine.
Hydrobromic acid	......	......	80.75	1 part hydrogen, 80 parts bromine.
Hydriodic acid	4.443	128	128	1 part hydrogen, 127 parts iodine.
Water	0.623	17.99	18	16 " oxygen, 2 " hydrogen.
Hydrogen sulphide	1.191	34.4	34	32 " sulphur, 2 " hydrogen.
Sulphurous oxide	2.247	64.9	64	32 " sulphur, 32 " oxygen.
Sulphuric oxide	3.01	86.9	80	32 " sulphur, 48 " oxygen.
Sulphuryl chloride	4.67	134.8	135	32 " sulphur, 32 " oxygen, 71 " chlorine.
Hydrogen selenide	......	......	80	78 " selenium, 2 " hydrogen.
Selenous oxide	4.03	116	110	78 " selenium, 32 " oxygen.
Hydrogen telluride	......	......	130	128 " tellurium, 2 " hydrogen.
Ammonia	0.597	17.2	17	14 " nitrogen, 3 " hydrogen.
Nitric oxide	1.039	30.0	30	14 " nitrogen, 16 " oxygen.
Nitrous oxide	1.520	43.9	44	28 " nitrogen, 16 " oxygen.
Phosphine	1.18	34.1	34	31 " phosphorus, 3 " hydrogen.
Phosphorous chloride	4.88	140.9	137.5	31 " phosphorus, 106.5 " chlorine.
Phosphorus oxichloride	5.40	155.9	153.5	31 " phosphorus, 16 " oxygen, 106.5 " chlorine.
Phosphorus sulphochloride	5.88	169.7	169.5	31 " phosphorus, 32 " sulphur, 106.5 " chlorine.
Triethylphosphine oxide	4.60	132.8	134	31 " phosphorus, 16 " oxygen, 72 " carbon, 15 " hydrogen.
Arsine	2.695	77.8	78	75 " arsenic, 3 " hydrogen.
Arsenous chloride	6.30	181.9	181.5	75 " arsenic, 106.5 " chlorine.

	d.	$d \times 28.88$	*M*.	Constituents.
Cacodyl chloride .	4.56	131.7	140.5	75 parts arsenic, 35.5 " chlorine, 24 " carbon, 6 " hydrogen.
Cacodyl cyanide .	4.63	133.7	131	75 " arsenic, 14 " nitrogen, 36 " carbon, 6 " hydrogen.
Arsenous iodide . .	16.1	464.8	456	75 " arsenic, 381 " iodine.
Antimonous chloride	7.8	224.7	228.5	122 " antimony, 106.5 " chlorine.
Triethylstibine . .	7.44	214.8	209	122 " antimony, 72 " carbon, 15 " hydrogen.
Bismuthous chloride	11.35	327.7	316.5	210 " bismuth, 106.5 " chlorine.
Boric chloride . .	3.942	113.8	117.5	11 " boron, 106.5 " chlorine.
Boric fluoride . .	2.312	66.8	68	11 " boron, 57 " fluorine.
Boric bromide . .	8.78	253.5	251	11 " boron, 240 " bromine.
Trimethylborine .	1.93	55.7	56	11 " boron, 36 " carbon, 9 " hydrogen.
Marsh-gas	0.557	16.1	16	12 " carbon, 4 " hydrogen.
Methyl fluoride . .	1.186	34.3	34	12 " carbon, 19 " fluorine, 3 " hydrogen.
Methyl chloride . .	1.736	50.1	50.5	12 " carbon, 35.5 " chlorine, 3 " hydrogen.
Methyl bromide . .	3.253	93.9	95	12 " carbon, 80 " bromine, 3 " hydrogen.
Methyl iodide . .	4.883	141	142	12 " carbon, 127 " iodine, 3 " hydrogen.
Chloroform . . .	4.2	121.3	119.5	12 " carbon, 1 " hydrogen, 106.5 " chlorine.
Carbon tetrachloride	5.24	151.3	154	12 " carbon, 142 " chlorine.
Carbon monoxide .	0.968	27.96	28	12 " carbon, 16 " oxygen.
Carbon dioxide . .	1.529	44.15	44	12 " carbon, 32 " oxygen.

	d.	$d \times 28.88$	*M.*	Constituents.
Carbon oxichloride .	3.505	101.2	99	12 parts carbon,
				16 " oxygen,
				71 " chlorine.
Carbon oxisulphide.	2.105	60.8	60	12 " carbon,
				16 " oxygen,
				32 " sulphur.
Carbon sulphide . .	2.645	76.4	76	12 " carbon,
				64 " sulphur.
Hydrocyanic acid .	0.948	27.4	27	12 " carbon,
				14 " nitrogen,
				1 " hydrogen.
Cyanogen chloride .	2.13	61.5	61.5	12 " carbon,
				14 " nitrogen,
				35.5 " chlorine.
Cyanic acid . . .	1.50	43.3	43	12 " carbon,
				14 " nitrogen,
				16 " oxygen,
				1 " hydrogen.
Methyl alcohol . .	1.12	32.3	32	12 " carbon,
				16 " oxygen,
				4 " hydrogen.
Methyl nitrate . .	2.64	76.2	77	12 " carbon,
				14 " nitrogen,
				3 " hydrogen,
				48 " oxygen.
Silicic fluoride . .	3.57	103.0	104	28 " silicon,
				76 " fluorine.
Silicic chloride . .	5.94	171.5	170	28 " silicon,
				142 " chlorine.
Silicic iodide . . .	19.1	551.4	536	28 " silicon,
				508 " iodine.
Siliconethyl . . .	5.13	148.1	144	28 " silicon,
				96 " carbon,
				20 " hydrogen.
Titanic chloride . .	6.84	197.5	192	50 " titanium,
				142 " chlorine.
Zirconic chloride .	8 15	235.4	232	90 " zirconium,
				142 " chlorine.
Stannic chloride .	9.20	265.7	260	118 " tin,
				142 " chlorine.
Tinethyl	8.02	231.6	234	118 " tin,
				96 " carbon,
				20 " hydrogen.
Tintriethyl chloride	8.43	243.4	240.5	118 " tin,
				35.5 " chlorine,
				72 " carbon,
				15 " hydrogen.

	d.	d/.0346	M.	Constituents.
Tintriethyl bromide	9.92	286.4	285	118 parts tin, 80 " bromine, 72 " carbon, 15 " hydrogen.
Tintriethyl iodide .	10.33	298.2	290	118 " tin, 127 " iodine, 36 " carbon, 9 " hydrogen.
Leadmethyl . . .	9.6	277.2	267	207 " lead, 48 " carbon, 12 " hydrogen.
Zincmethyl . . .	3.29	95.0	95.2	65.2 " zinc, 24 " carbon, 6 " hydrogen.
Zincethyl	4.62	123	123.2	65.2 " zinc, 48 " carbon, 10 " hydrogen.
Mercurymethyl . .	8.29	239.4	230	200 " mercury, 24 " carbon, 6 " hydrogen.
Mercuryethyl . .	9.97	287.8	258	200 " mercury, 48 " carbon, 10 " hydrogen.
Mercuric chloride .	9.8	283	271	200 " mercury, 71 " chlorine.
Mercuric bromide .	12.16	3.51	360	200 " mercury, 160 " bromine.
Mercuric iodide . .	16.2	468	454	200 " mercury, 254 " iodine.
Osmic oxide . . .	8.9	257	263.2	199.2 " osmium, 64 " oxygen.
Chromic acichloride	5.55	159	155	52 " chromium, 32 " oxygen, 71 " chlorine.
Molybdenic chloride	9.46	273	269.5	92 " molybdenum, 177.5 " chlorine.
Tungsten chloride .	12.7	366	361.5	184 " tungsten, 177.5 " chlorine.
Tungsten hexachloride	13.2	383	397	184 " tungsten, 213 " chlorine.
Tungsten oxichloride	11.84	342	342	184 " tungsten, 16 " oxygen, 142 " chlorine.
Vanadic tetrachloride	6.69	193	196.3	51.3 " vanadium, 142 " chlorine.
Vanadic acichloride	6.11	176	173.8	51.3 " vanadium, 16 " oxygen, 106.5 " chlorine.

	$d.$	$d \times 28.88$	$M.$	Constituents.
Niobic chloride . .	9.6	277	272.5	95 parts niobium, 177.5 " chlorine.
Niobic acichloride .	7.88	228	217.5	95 " niobium, 16 " oxygen, 106.5 " chlorine.
Tantalic chloride .	12.9	372	359.5	182 " tantalum, 177.5 " chlorine.
Aluminic chloride .	9.35	270	267.6	54.6 " aluminium, 213 " chlorine.
Aluminic bromide .	18.6	537	534.6	54.6 " aluminium, 480 " bromine.
Aluminic iodide . .	27	780	816.6	54.6 " aluminium, 762 " iodine.
Ferric chloride . .	11.39	329	325	112 " iron, 213 " chlorine.

This list contains compounds of thirty different elements; and, by means of these compounds, supposing that they contain at least one of their elements in the smallest possible quantity, we can determine the atomic weights of the elements concerned. It will be seen, however, that, whereas the hypothesis of Avogadro furnishes us with a principle which enables us to state positively what the molecular weight of any gaseous compound is, it does not furnish a means for the determination of atomic weights directly. After examining the various compounds of an element, we select that one which contains the smallest quantity of the element in the molecule, and then, without proof of any kind, we say this smallest quantity represents the atom. Thus it is evident that the atomic weights, as determined by this method, rest upon a more or less doubtful basis. For practical purposes, however, this is not a serious matter; inasmuch as, although we cannot assert that the weight found really represents the atomic weight, we can assert that it represents the weight of that portion of the element which conducts itself as an atom, *i.e.*, throughout the whole series of changes which it undergoes in its compounds it is indivisible.

Other Proofs of the Fact that the Molecules of Elements contain more than one Atom.—It has been stated above that the molecules of elements contain, in almost all cases, more than one atom; and it has been shown that, if the hypothesis of Avogadro be accepted, we are necessarily led to this conclusion by a simple consideration of the molecular weights of elements and their compounds. The question naturally arises: Are there other evidences, independent of Avogadro's hypothesis, of the fact that the molecules of elements consist of more than one atom? There are.

A number of the elements, as we ordinarily meet with them in the free state, conduct themselves as comparatively neutral bodies. Take, for instance, hydrogen. As a gas, this element possesses very little affinity for most other elements and compounds. We may bring it in immediate contact with most substances without effecting any change whatever in these substances. If, however, we set it free from one of its compounds, and, at the moment it is set free, allow it to act upon some other body, we find that it is a comparatively active element, capable of effecting very material changes in other substances. The same is true of oxygen, nitrogen, and other elements. They are much more active in the *status nascendi* than in the free state. How shall we explain this? This can be done most readily by supposing the molecules of these elements, in the free state, to contain more than one atom bound together by chemism. Now, if it be required that an element thus constituted shall combine with another body, it is first necessary that the force which holds together the atoms be overcome; the atoms must be torn asunder before they can act as atoms; or, in other words, a decomposition must be effected before the required combination can take place.

Sometimes the attraction exerted by an atom of one element for an atom of another is so strong that this decomposition is effected, and the combination then takes place. Thus, if we bring hydrogen and chlorine together, both in the free state, they combine. In this case, the chlorine atom attracts the hydrogen atom more strongly than the hydrogen atom attracts its fellow, or the chlorine atom its own chlorine atom. On the other hand, numerous instances of the opposite kind might be adduced. One will suffice for the purpose of illustration. When hydrogen gas is passed through nitric acid no change takes place. But, if we dissolve zinc in nitric acid, a portion of the acid is decomposed by the hydrogen evolved. The hydrogen atoms, set free from the nitric acid, find the acid present, and act upon it in preference to combining to form free hydrogen; the elements in combination with nitrogen are forcibly removed and the hydrogen takes their place, forming ammonia.

Ordinary oxygen contains two atoms in the molecule. Ozone, another variety of oxygen, has the density 1.658, from which we find its molecular weight = 48. Now as the atomic weight of oxygen, according to previous determinations, is 16, it follows that the molecule of ozone contains three atoms. The difference between the two forms of oxygen is thus readily seen. Ozone is comparatively unstable. It gives up its extra atom with great ease to bodies with which it comes in contact, and causes thus an energetic oxidation. When heated up to 300°, it is also decomposed, forming ordinary oxygen, and then an increase of volume is observed. In this case, if no foreign body be present with which the liberated atom can unite, it unites with another atom of the same kind. When it acts upon other bodies, the original volume of the gas remains unchanged. It would then appear that, in the molecule of ozone, two of the atoms are held together by a stronger force than that which binds the third characterizing atom; or, rather, that the two atoms of the molecule of ordinary oxygen are held together more firmly than the three atoms in the molecule of ozone. Here then again the different actions of the two varieties can be best explained by supposing in each case the molecule to consist of more than one atom.

These and other similar considerations serve to strengthen the conclusion which was logically deduced from Avogadro's hypothesis, and hence, in turn, to increase the probability that the hypothesis is the expression of a natural law.

Molecular Formulas of Gaseous Compounds.—When the atomic weights of the elements are once determined, the rule of Avogadro, taken in conjunction with analysis, is sufficient to enable us to establish the molecular formulas of gaseous chemical compounds; a problem, the solution of which without this rule is in many cases exceedingly difficult, and, indeed, at times impossible. Let us suppose the atomic weights of carbon (12), hydrogen (1), and oxygen (16) to be known. We analyze a certain compound, and find that it contains 37.50 per cent. carbon, 12.50 per cent. hydrogen, and 50.00 per cent. oxygen. This gives the atomic proportion 1 of carbon, 4 of hydrogen, and 1 of oxygen; and hence the simplest formula we can assign to the compound is CH_4O. But there is nothing thus far to prevent our acceptance of one of the formulas $C_2H_8O_2$ or $C_3H_{12}O_4$, etc., all of which satisfy the results of the analysis. We now determine the molecular weight by Avogadro's rule, and find it to be 32; and, as the sum of the weights of the atoms in a molecule of a compound of the formula CH_4O is 32, we recognize this latter as the correct formula.

Apparent Exceptions.—All formulas of chemical compounds at present employed are intended to represent molecules of the compounds. They are molecular formulas. They represent those amounts of the bodies which, in a gaseous condition, would occupy the same space as a molecule of hydrogen. If we take two volumes of hydrogen as the standard of comparison, then the formulas of compounds represent two volumes of the same size. To this there are apparent exceptions. When ammonia acts upon hydrochloric acid, the two gases combine in the proportion of 1 vol. of the one to 1 vol. of the other, forming a solid compound which contains 26.17 per cent. nitrogen, 7.48 per cent. hydrogen, and 66.35 per cent. chlorine. This gives the atomic proportion 1 nitrogen, 4 hydrogen, and 1 chlorine; and the simplest formula we can assign to the compound, provided the atomic weights of nitrogen, hydrogen, and chlorine are respectively 14, 1, and 35.5, is NH_4Cl. On now determining the molecular weight by Avogadro's rule, this is found to be 26.75, or half of that required by the above formula. Evidently, it is impossible for a molecule made up of chlorine, nitrogen, and hydrogen, with the atomic weights above assigned to them, to have as small a weight as 26.75; and, to satisfy the results of this determination, we would be obliged to write the formula $N_{\frac{1}{2}}\,H_2\,Cl_{\frac{1}{2}}$, and thus accept the existence of half-atoms, which, according to the definition of atoms, is impossible. We might also imagine the atomic weight of nitrogen and chlorine, as already determined, to be just twice too great; for, if we assign to nitrogen the atomic weight 7, and to chlorine 17.7, we could write the formula of the compound NH_2Cl, and this compound would have the molecular weight 26.7, as determined by Avogadro's method. On the other hand, if 7 is the atomic weight of nitrogen, and 17.7 that of chlorine, then in all other compounds of nitrogen or chlorine, in which one atom has been supposed to exist in the molecule, we must necessarily accept the existence of two atoms in the molecule. But then all these compounds would not come under Avogadro's rule. Hence we see that the compound NH_4Cl appears to be an exception, and, if no satisfactory explanation can be found to account for this case, its existence is fatal to the rule. A satisfactory explanation can be offered, however, as follows.

If it can be proved that the vapor obtained from the compound NH_4Cl is not the vapor of this compound, but a mixture of the vapors of its constituents NH_3 and HCl, the case becomes a very simple one. Without entering into details, it may be mentioned that the results of the experiments made upon this subject have justified the assumption that, when the compound NH_4Cl is heated up to a temperature sufficiently high to cause its conversion into vapor, it becomes resolved into its constituents NH_3 and HCl; and that, when this mixture of two vapors is again cooled down, the two again unite to form the original compound.

As NH_3 and HCl combine volume to volume, so the mixture of the two gases, obtained by heating NH_4Cl, consists of equal volumes of the two; and the specific gravity of this mixed vapor would be the mean of the specific gravities of its constituents. The specific gravity of NH_3 is 0.597, that of HCl is 1.247; the specific gravity of a mixture of the two would be $\frac{0.597+1.247}{2}=0.922$; and this specific gravity, if supposed to be that of a chemical compound, would lead to the molecular weight 26.6. The number 0.922 is, indeed, that found as the specific gravity of the vapor of NH_4Cl, and it will thus be seen that the fact can be satisfactorily explained without giving up our belief in the correctness of Avogadro's hypothesis.

The compound PCl_5 was also, at one time, supposed to form an exception to the rule. The specific gravity of its vapor was found to be 3.66, from which was calculated the molecular weight 105.7, half that required by the formula PCl_5. It has been shown, however, that above a certain temperature the molecule of PCl_5 breaks up into a molecule of PCl_3 and a molecule of Cl_2. The vapor from PCl_5 is a mixture of two vapors, and the mean specific gravity of the two is the specific gravity found. The specific gravity of the vapor of PCl_3 is 4.88; that of Cl is 2.45; mean specific gravity $\frac{4.88 + 2.45}{2} = 3.666$. In this case it has further been shown that the breaking up of the molecule takes place gradually; for the specific gravity of the vapor decreases from 5.08 to 3.66, as the temperature is elevated from 182° to 300°, at which latter temperature the decomposition appears to be complete, no further decrease in specific gravity being noticed when the vapor is heated still higher.

It has further, recently, been shown that when the specific gravity of the vapor of PCl_5 is determined in the presence of PCl_3, its dissociation is prevented, and the specific gravity found is that which theory requires for a compound of the formula PCl_5. The mean result of seven determinations was 7.226, whereas, the theory requires 7.217. From this it is evident that the hypothesis of Avogadro is as valid for the compound PCl_5 as for other compounds.

A third example of this kind of decomposition by increase of temperature is met with in the case of the compound NO_2. This body, at a low temperature, consists of colorless crystals. At a slightly elevated temperature these crystals change to a yellow liquid. The liquid boils at 20–30°, and is then converted into a gas of a reddish-brown color, and, as the temperature of the gas increases, the intensity of the color also increases. The specific gravity of the gas decreases with this elevation of temperature; hence, it is supposed that the body, at a low temperature, must be represented by the formula N_2O_4, but that the molecule is broken up by an increase of temperature, forming two molecules of NO_2. The latter is strongly colored, and the more of it there is present in the mixture, the more intense will be the color of the gas.

Among chemical compounds there are very few indeed that conduct themselves in the manner of the three just described. As regards some of these, good proof can be given of the fact that their molecules are broken up by the conversion into vapor, and hence, the apparently abnormal specific gravities observed for these vapors find a simple explanation. As regards others, although positive proof to the same effect may indeed be lacking as yet, still strong indications are presented that the abnormal densities may be referred to the same cause. So that, up to the present, not only is no fact known that speaks strongly against Avogadro's hypothesis, but, on the contrary, new developments, increased knowledge are constantly tending to strengthen it. It forms, to-day, by far the most reliable means for the determination of molecular weights of compounds and elements; and we have seen how, secondarily, it aids us in determining atomic weights. But, in order that it may be useful, it is necessary that the compound which we desire to study shall be capable of conversion into vapor, or, if it be an element under consideration, that at least one of the compounds of this element be gaseous or volatile. Only a comparatively small number of compounds satisfy these conditions, and of the 64 elements, only 30 (see List, pp. 45–49) enter into the composition of these compounds. With no other means, then, at our command, the work would be incomplete. It is necessary that some other method should be introduced which shall be applicable to those elements not covered by Avogadro's rule, *i. e.*, those elements which are themselves incapable of conversion into vapor, and which do not enter into the composition of gaseous or volatile compounds.

III.

EXAMINATION OF SOLID ELEMENTS AND COMPOUNDS.

Specific Heat.—It has been noticed that, when equal weights of different substances are exposed to the heat from the same source, they will have different temperatures at the end of the same period of time. From this we conclude that, to raise equal weights of different substances through the same number of degrees of temperature, different quantities of heat are necessary. Given exactly the same heating power, it takes about 32 times as long to raise the temperature of a pound of water ten, twenty, or thirty degrees, as it takes to raise the temperature of a pound of mercury the same number of degrees; or it takes 32 *times as much heat* to raise the temperature of a pound of water ten, twenty, or thirty degrees as it takes to raise the temperature of the pound of mercury the same number of degrees. The quantity of heat required to raise the temperature of a given weight of any substance a given number of degrees, as compared with the quantity of heat required to raise the temperature of the same weight of water the same number of degrees, is called the specific heat of the substance. The quantity of heat required to raise the temperature of a pound of water one degree Centigrade, may be conveniently adopted as the thermal unit. We then speak of the specific heat of water as $= 1$; and the specific heat of any other body is the relative quantity of heat necessary to raise the temperature of a pound of this body one degree Centigrade, taking the above thermal unit as the standard. The specific heat of mercury, according to the results of the experiment mentioned, is 0.03332; that of gold is found to be 0.03244, etc. etc. The meaning of these numbers will be readily seen.

Relations between Specific Heat and Atomic Weight.—Now, when the solid elements are examined with reference to their specific heats, a very simple relation is found to exist between the numbers expressing the specific heats and the atomic weights. This relation will be made clear by a consideration of a few cases actually examined:—

Element.	Specific heat.	Atomic weight.
Silver	0.0570	108
Zinc	0.0955	65.2
Cadmium	0.0567	112
Copper	0.0952	63.4
Tin	0.0562	118

It will be seen by an examination of this table that the atomic weights are inversely proportional to the specific heats. We have—

$$108 : 65.2 :: 0.0955 : 0.0570;$$
$$112 : 63.4 :: 0.0952 : 0.0567;$$
$$108 : 118 :: 0.0562 : 0.0570, \text{ etc. etc.}$$

These proportions are only approximately correct; but it must be remembered that the means for the determination of atomic weights are capable of much greater refinement than those employed for the determination of specific heats. There is much greater liability of error in the latter determinations than in the former. Hence such slight variations from absolute agreement in these proportions can occasion no surprise. The agreement is sufficiently close to indicate a decided and undoubted connection between the two sets of numbers. This connection may be stated in another way: The product of the atomic weight into the specific heat is a constant quantity for the elements examined. Thus in the above cases:—

$$108 \times 0.057 = 6.15$$
$$65.2 \times 0.0955 = 6.22$$
$$112 \times 0.0567 = 6.35$$
$$63.4 \times 0.0952 = 6.03$$
$$118 \times 0.0562 = 6.63$$

For the same weights, then, the quantities of heat necessary to elevate the temperature of the elements one degree vary. The quantity necessary to elevate the temperature of an atom one degree would, of course, be represented by the variable quantity multiplied by the atomic weight; and this product, in the cases cited, we find to be represented by a constant.

Investigations of Dulong and Petit.—In the year 1819 attention was first called to the above relation by Dulong and Petit; and, having examined a large number of elements, they felt justified in propounding the law: *The atoms of all elementary bodies have exactly the same capacity for heat.* This is simply a generalization from the facts stated, and is another way of stating that, to raise the temperature of atoms one degree, the same quantity of heat is always necessary.

If the law propounded is in reality a law, it will be readily seen that a new means is given for the determination of the atomic weights of elements of which we can know the specific heat. If we assume that the constant number obtained by multiplying the specific heats by the atomic weights is 6.25, which is about the average of the different values found, then it is plain that, if we divide this number by the specific heat of an element, we shall obtain a number which approximately represents the atomic weight. If we call the atomic weight A, and the specific heat H, the following formula will express the relation:—

$$A = \frac{6.25}{H}.$$

In order that this might hold good for all the elements investigated by Dulong and Petit, they found it necessary to change the atomic weights of four of the metals; just as it had been necessary to change certain of the atomic weights in order that Avogadro's hypothesis might hold good in all cases. But, as these atomic weights had been determined purely empirically, and thus rested upon a questionable basis, there could be no serious objection to the change. Notwithstanding the simplicity of the law, its validity was not, however, immediately acknowledged.

Investigations of Neumann and Regnault.—Twelve yeas later (1831), Neumann published investigations on the specific heat of chemical compounds, and showed that, for bodies of similar composition, the specific heats are inversely proportional to the molecular weights of the compounds; or the molecules of different compounds have equal capacity for heat; *i. e.*, for bodies of similar composition, the product of the molecular weight (M) into the specific heat (H) is a constant quantity. For example, the specific heat of lead iodide is 0.0427; that of lead bromide is 0.0533; that of lead chloride is 0.0664; the molecular weights of these compounds are respectively 461, 367, and 278. The products $M \times H$ are as follows:—

For lead iodide . .	$461 \times 0.0427 = 19.68$
“ bromide . .	$367 \times 0.0533 = 19.56$
“ chloride . .	$278 \times 0.0664 = 18.46$

Further, the specific heat of barium chloride is 0.0902; that of strontium chloride is 0.1199; that of calcium chloride is 0.1642. The molecular weights of these compounds are respectively 208, 158.5, and 111. The products $M \times H$ are—

For barium chloride .	$208 \times 0.0902 = 18.76$
“ strontium chloride .	$158.5 \times 0.1199 = 19.00$
“ calcium chloride .	$111 \times 0.1642 = 18.22$

Subsequently, similar investigations were carried out in connection with a larger number of compounds, and it is particularly to the labors of Regnault (1840) that the development of this branch of the subject is due. The result attained may be stated concisely thus: *The elements possess essentially the same specific heat whether they exist in a free state or are in combination.*

To show how this conclusion may be deduced from known facts, let us take again the case of lead iodide. Lead has the specific heat 0.0307, iodine 0.0541. Multiplying by the atomic weights, we have $0.0307 \times 207 = 6.35$; and $0.0541 \times 127 = 6.87$; but, as can be determined, there are two atoms of iodine in the molecule of lead iodide, hence the atomic heat 6.87 must be multiplied by 2, which gives 13.74. To raise the constituents of lead iodide one degree in temperature would then require an amount of heat represented by the number $6.35 + 13.74 = 20.09$, and we have found that the amount of heat necessary to raise lead iodide as a compound one degree in temperature is 19.68. As these results may be looked upon as coincident, it follows that the specific heat of the elements in this case is the same whether the elements be in combination or in the free state.

Determination of Atomic Weights by a Study of the Specific Heat of Compounds.—Adopting the principle involved in the above remarks, we see that a study of the specific heat of compound bodies may aid us in the determination of atomic weights; for we may ascertain the specific heat of an element even where this cannot be determined directly. It is difficult, for instance, to ascertain the specific heat of gaseous elements directly, and yet, as these elements form solid compounds, the specific heat of these latter may be determined, and thus, indirectly, that of the gaseous elements.

To illustrate by an example, let us consider the case of chlorine. Suppose it be required to determine the atomic weight of this element by means of specific heat determinations. We cannot determine the specific heat of the element directly. It forms compounds, however, with other elements, the specific heats and atomic weights of which may be determined. It combines with lead. The specific heat of lead is found to be 0.0307, which, according to the law of Dulong and Petit, gives the atomic weight 207. Now, in lead chloride, we find that 207 parts by weight of lead are combined with 71 parts by weight of chlorine; or, with one atom of lead, there is combined an amount of chlorine weighing 71 times as much as an atom of hydrogen. But we do not know how many atoms of chlorine this weight represents. It cannot be less than 1, but it may be 2, 3, 4, or more atoms, as far as we know. We determine the specific heat of lead chloride, and find it to be 0.0664. We have assumed that the molecular heat of a compound (*i.e.*, the product of the molecular weight into the specific heat) is equal to the sum of the atomic heats (*i.e.*, the product of atomic weight into the specific heat) of the atoms contained in the compound; or—

$$M \times H = A \times H + A' \times H' + A'' \times H'' \ldots .$$

But as the products $A \times H$, $A' \times H'$, $A'' \times H''$ have been shown to be constant and equal to about 6.25, we may simplify this equation as follows:—

$$M \times H = n 6.25\,;$$

and from this equation, M and H being known, we can determine the value of n, or the number of atoms contained in the molecule.

In the case under consideration we would have:—

$$278 \times 0.0664 = n6.25;$$
$$18.46 = n6.25;$$
$$n = 3.$$

We then conclude that in the molecule (278 parts) of lead chloride there are contained three atoms. But we know that there is one atom of lead; hence, there must be two atoms of chlorine; and, as two atoms weigh 71, the atomic weight of chlorine is 35 5, the same as that found by means of Avogadro's method.

Further, we have other compounds in each of which 71 parts of chlorine are combined with a certain quantity of another element, and the molecular heat of which is the same as that of lead chloride. From the latter fact we conclude that there are also three atoms contained in the molecules of these compounds, and hence, that quantity of an element which, in these compounds, is combined with 71 parts of chlorine, represents the atomic weight. Thus, we have for the molecular heat of barium, strontium, and calcium chlorides 18.76, 19.00 and 18.22, respectively, numbers which may be considered the same as 18.46, the molecular heat of lead chloride; and in these compounds there are 137 parts barium, 87.5 parts strontium, and 40 parts calcium, combined with 71 parts chlorine. We hence conclude that 137, 87.5 and 40 are respectively the atomic weights of barium, strontium, and calcium, although direct determinations of the specific heat have been made in only two of these cases.

Of course, just as we have thus indirectly determined the atomic weights of certain elements, we can also determine the unknown specific heats of these same elements by a slight variation of the process. Take lead chloride. The molecular heat of this compound is 18.46; the atomic heat of lead is 6.35; hence, we have $18.46 - 6.35 = 12.11$, for twice the atomic heat of chlorine, there being two atoms of chlorine contained in the compound. This gives the atomic heat $\frac{12.11}{2} = 6.06$ for chlorine; and dividing by the atomic weight, we obtain $\frac{6.06}{35.5} = 0.1707$, which, accordingly, would represent the specific heat of chlorine, if the gases were subject to precisely the same law as solids.

By processes like those described, the atomic weights of a number of the elements have been determined, and, in many cases, the results obtained have been considered decisive.

The following tables (I.) of elements, and (II.) of compounds, contain the numbers actually obtained and the results deduced from them. The numbers under H are those representing the specific heats of the elements; those under A are the atomic weights as determined by analytical methods, aided by the rule of Avogadro, or that of Dulong and Petit; finally, in the last column, is the product of the atomic weight into the corresponding specific heat $A \times H$, called, for convenience sake, the atomic heat.

	H.	A.	$A \times H$.
Lithium	0.941	7	6.6
Sodium	0.293	23	6.7
Magnesium	0.250	24	6.0
Aluminium	0.214	27.4	5.9
Silicon	0.173	28	4 8
Phosphorus	0.174	31	5.4
Sulphur	0.178	32	5.7
Potassium	0.166	39	6.5
Calcium	0.170	40	6.8
Chromium	0.100	52	5.2
Manganese	0 122	55	6.7
Iron	0.114	56	6.4
Cobalt	0.107	59	6.2
Nickel	0.109	59	6.4
Copper	0.0952	63.4	6.0
Zinc	0.0955	65.2	6.2
Arsenic	0.0814	75	6.1
Selenium	0.0746	79.4	5.9
Bromine (solid) . . .	0 0843	80	6.7
Molybdenum	0 0722	92	6.6
Ruthenium	0.0611	104.4	6.4
Rhodium	0.0580	104.4	6.1
Palladium	0.0593	106.6	6.3
Silver	0.0570	108	6.2
Cadmium	0.0567	112	6.4
Indium	0.0570	113.4	6.5
Tin	0.0562	118	6.6
Antimony	0.0508	122	6.2
Iodine	0.0541	127	6.9

	H.	A.	A × H.
Tellurium	0.0474	128	6.1
Tungsten	0.0334	184	6.1
Gold	0.0324	197	6.4
Platinum	0.0324	197.4	6.4
Iridium	0.0326	198	6.5
Osmium	0.0311	199.2	6.2
Mercury	0.0317	200	6.3
Thallium	0.0335	204	6.8
Lead	0.0307	207	6.4
Bismuth	0.0308	210	6.5

The following are some of the compounds which have been employed for the purpose of determining the atomic weights of elements. The numbers under *H* are those representing the specific heats of the compounds; those under *M* are the molecular weights; the products $M \times H$ are the so-called molecular heats; *n* represents the number of atoms in the molecule of the compound.

	$H.$	$M.$	$M \times H.$	$n.$	$\frac{M \times H}{n}$
$CoAs_2$	0.0920	209	19.2	3	6.4
Ag_2S	0.0746	248	18.5	3	6.2
Cu_2S	0.1212	158.8	19.2	3	6.4
HgS	0.052	232	12.1	2	6.1
NiS	0.1281	91	11.6	2	5.8
PbS	0.053	239	12.7	2	6.4
SnS	0.0837	150	12.6	2	6.3
SnS_2	0.1193	182	21.7	3	7.2
$AgCl$	0.0911	143.5	13.1	2	6.6
$CuCl$	0.1383	98.9	13.7	2	6.9
KCl	0.1730	74.6	12.9	2	6.5
$LiCl$	0.2821	42.5	12.0	2	6
$NaCl$	0.2140	58.5	12.5	2	6.3
$BaCl_2$	0.0896	208	18.6	3	6.2
$CaCl_2$	0.1642	111	18.2	3	6.1
$SrCl_2$	0.1199	158.5	19.0	3	6.3
$HgCl_2$	0.0689	271	18.7	3	6.2
$MgCl_2$	0.1946	95	18.5	3	6.2
$MnCl_2$	0.1425	126	18.0	3	6.0
$PbCl_2$	0.0664	278	18.5	3	6.2

Exceptions to the Law of Dulong and Petit.—On examining these tables, we are struck by the fact that the product, $A \times H$, in the first, and the quotient, $\frac{M \times H}{n}$, in the second—although assumed to be constant in value—show a very considerable variation from the mean value, 6.25. For a large number of these cases, we are justified in concluding that the variation is due to the errors of observation in consequence of the imperfections of the methods employed for the determination of specific heat. Indeed, in all the cases cited in the above tables, the variations are hardly great enough to lead us to suspect the incorrectness of the law of Dulong and Petit. If, however, we consider the elements carbon, boron, and silicon, we shall find that entirely different results are reached, and we are compelled to admit that, for these elements at least, the law does not appear to hold good. This will be best seen by means of the following table, in which H is the specific heat; t, the temperature at which the determination was made; A, the atomic weight; and $A \times H$, the atomic heat. As these three elements form the most marked exceptions to the law, all the most reliable determinations of their specific heats that have been made by different observers are given, for reasons which we shall presently see.

	H.	*t.*	*A.*	$A \times H$.
Boron (crystallized)	0.230	+20 to 51°	11	2.5
" "	0.244	+10 " 100	"	2.7
Carbon:				
a. Diamond	0.095	at 0	12	1.1
"	0.144	" 50	"	1.7
"	0.145	+24 to 70	"	1.7
"	0.147	+ 9 " 98	"	1.8
"	0.191	at 100	"	2.3
"	0.236	" 150	"	2.8
"	0.279	" 200	"	3.3
b. Blast-furnace graphite	0.165	+20 to 52	"	2.0
" "	0.192	+23 " 66	"	2.3
" "	0.197	+12 " 98	"	2.4
c. Natural graphite	0.144	0 " 34	"	1.7
" "	0.174	+20 " 52	"	2.1
" "	0.192	+24 " 67	"	2.3
" "	0.197	0 " 100	"	2.4
" "	0.198	+15 " 99	"	2.4
d. Gas-coal	0.185	+ 21 " 52	"	2.2
"	0.201	+22 " 70	"	2.4
"	0.200	+16 " 100	"	2.4
e. Charcoal (veg.)	0 241	+10 " 98	"	2.9
f. " (animal)	0.261	+19 " 99	"	3.1
Silicon:				
melted	0.138	+20 " 50	28	3.9
"	0.166	+20 " 100	"	4.6
crystallized	0.165	+20 " 50	"	4.6
"	0.173	+20 " 100	"	4.8

Here then it will be observed that not only do the atomic heats of the three elements vary markedly from the constant 6.25, but for different conditions of the same element decided variations take place. In these cases there can be no thought that the determinations are incorrect. They have been made repeatedly by the most careful experimenters, but always with the same results; and, as already stated, we are now forced to admit that the three elements—carbon, boron, and silicon—form undoubted exceptions to the so-called law of Dulong and Petit, as this law has been stated. But shall we then without further inquiry abandon the law as useless? This question has been answered in the affirmative by some; but the majority of chemists at present accept it with the restrictions necessarily imposed by the nature of the facts, and employ it in the determination of atomic weights, not forgetting that implicit confidence cannot be placed in the results thus obtained. It is chiefly useful as an aid to the other methods, and as such it is very useful. If we examine those elements carefully which form more or less marked exceptions to the law, we shall find that they all have small atomic weights; they belong to the class of bodies known as non-metals; and they are either gases themselves or they form compounds that are gases, or, at least, volatile. By calculation, the atomic heat of hydrogen has been found to be about 2.3; that of oxygen about 4; that of fluorine about 5; that of nitrogen about 5. Further, we have seen that the atomic heat of carbon is 1.1 to 3.1; of silicon 3.9 to 4.8; of boron 2.5 to 2.7; of sulphur 5.7; of phosphorus 5.4. Arranging these elements in the order of increasing atomic weights, we have—

	A.	Atomic heat.
Hydrogen	1	2.3
Boron	11	2.5–2.7
Carbon	12	1.1–3.1
Nitrogen	14	5 –5.5
Oxygen	16	4
Fluorine	19	5
Silicon	28	3.9–4.8
Phosphorus	31	5.4
Sulphur	32	5.7

This list includes all the elements that, in their atomic heats, do not comply with the law of Dulong and Petit. It will be seen that the largest atomic weight represented is that of sulphur, viz., 32. Among the elements with higher atomic weights no exceptions have as yet been noticed, and hence the law is looked upon as valid for these latter. We may then say that, for elements with high atomic weights, specific heat determinations may be employed for the determination of atomic weights. But these elements are just the ones that we cannot reach by means of Avogadro's rule, whereas those noticed above as exceptions can be; hence the two methods supplement each other, and, as far as they may be relied upon, enable us to determine the atomic weights of all the elements.

Although we have considered carbon, silicon, and boron as exceptions to the law of Dulong and Petit, very recent investigations show that, strictly speaking, they are not exceptions. The specific heats of these elements increase gradually from the lowest temperature to certain points, when they remain constant for any further increase in temperature. The point for carbon and boron* is in the neighborhood of 600°; that for silicon about 200°. At these temperatures, and above them, the elements have the following specific heats: carbon 0.46; boron 0.50; silicon 0.205. The products obtained by multiplying these figures by the atomic weights 12, 11, and 28 are 5.5, 5.5, and 5.8; so that carbon, boron, and silicon are not exceptions. The law of Dulong and Petit, however, is a little more complicated than we have stated it to be, and should have the following form:—

The specific heats of the elements vary with the temperature; but for every element there is a point, T, above which the variations are very slight. The product of the atomic weight into the constant value of the specific heat is nearly a constant, lying between 5.5 and 6.5.

It was further found that all the opaque modifications of carbon have the same specific heat, and above 600° this is the same as that stated above, viz., 0.46.

To account for the variations in the specific heats of the elements, it has been suggested that we cannot in most cases determine the true specific heat. This is only that heat which goes to increase the temperature. In measuring specific heats, we usually deal with a complex quantity, viz., that heat which raises the temperature, together with that which performs internal work and that which performs external work. In the cases of solids and liquids, the external work performed is very small. The internal work is probably different in different cases, and may amount to considerable. The fact, that the specific heats of so many elements give with the atomic weights of these elements the same product, indicates that in these cases the external work, like the specific heat, is inversely proportional to the atomic weights. It is perfectly evident, according to this, that, if the amount of internal work varies in different elements, the specific heat will also vary in such a way as to seem to conflict with the law. It remains then for the future to show how specific heat determinations can be made which shall be independent of the internal and external work. When this can be done, it is probable that the law of Dulong and Petit will be found to be a perfect law, without exceptions of any kind.

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* According to Hampe (Annalen der Chemie, 183, 75), the substance which has always been looked upon as the element boron is not the element. The black crystals of Wöhler have the composition AlB_{12}, and the yellow crystals the composition $C_2Al_3B_{48}$. In the light of these results it appears then that, as yet, we do not know the specific heat of boron.

ISOMORPHISM AS FURNISHING A MEANS FOR DETERMINING ATOMIC WEIGHTS.—Another means, once considered valuable, for determining atomic weights is found in connection with isomorphism. It has long been known that substances of entirely different composition have the same crystalline form. This was explained by Mitscherlich (1819) by supposing that an equal number of atoms in different molecules gave rise to the same crystalline form. A little later, he proposed the following statement as probably representing the law of isomorphism:—

> *An equal number of atoms, united in the same way, give the same crystalline form; and this crystalline form is independent of the chemical nature of the atoms, being only dependent on their number and arrangement.*

If this law were strictly true, it is plain that we should in many cases be able to determine atomic weights by its aid. A few examples will illustrate this method:—

The two substances $BaCl_2+2H_2O$ and $BaBr_2 2+H_2O$ are isomorphous. We may assume, then, that their molecules contain the same number of atoms, and, if we know the atomic weights of the constituents of the molecule $BaCl_2+2H_2O$, we can easily determine the atomic weight of the Br in the molecule $BaBr_2+2H_2O$. Further, the compounds CuAgS and CuCuS are isomorphous. Assuming that the molecules of each contain the same number of atoms, and knowing the atomic weights of copper and sulphur, we obtain very readily the atomic weight of silver.

It cannot be denied that this method has been of service in the establishment of the atomic weights. Nevertheless, it requires but a few examples to prove that the results reached by means of it are not perfectly reliable.

The salts $BaMn_2O_8$, Na_2SO_4, and Na_2SeO_4 are isomorphous, and yet the best methods for determining formulas show that those given are the correct ones. If we were, in these cases, to assume that the number of atoms in each of the molecules is the same, we would reach results at variance with those obtained by our most reliable means. We see thus that, if the isomorphism of salts is employed as a means for the determination of atomic weights, the results must be looked upon as doubtful.

IV.

PROPERTIES OF THE ELEMENTS AS FUNCTIONS OF THEIR ATOMIC WEIGHTS.

Natural Groups of Elements.—If we examine the list of elements and their atomic weights, we find that there is a number of well-marked groups, indicating some connection between the atomic weights and properties of the elements. Among these may be mentioned chlorine, bromine, and iodine; sulphur, selenium, and tellurium; lithium, sodium, and potassium. Arranging these according to their atomic weights, we have:—

Cl	35.5	S	32	Li	7
Br	80	Se	79.5	Na	23
I	127	Te	128	K	39

If, in each of these groups, we add together the atomic weights of the first and last elements, and divide this sum by 2, we obtain very nearly the atomic weights of the middle members of the series: $\frac{35.5 + 127}{2} = 81.25$, $\frac{32 + 128}{2} = 80$, $\frac{7 + 39}{2} = 23$. We see, also, that the elements, whose atomic weights are thus closely connected, are themselves very closely allied in their properties. Considerations of this kind have led chemists, from time to time, to examine the atomic weights more closely, and, as a result of these examinations, it has been found that the connection above indicated is much more general than was at first supposed. A number of schemes have been devised for the purpose of showing this connection clearly, some of which are certainly worthy of attention. We shall consider here the schemes of D. Mendelejeff* and Lothar

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* Zeitschrift für Chemie, 1869, 405, and Annalen d. Ch. u. Pharm., 8 Suppl. 133.

Meyer,* as they embody all that is good of other schemes and are themselves comparatively perfect.

The Scheme of Mendelejeff.—Mendelejeff first calls attention to the fact that, if all the light elements with atomic weights from 7 to 36 are arranged *in the order of their atomic weights*, the following remarkable table is obtained:—

Li = 7; Be = 9.4; B = 11 ; C = 12; N = 14; O = 16; Fl = 19.
Na = 23; Mg = 24 ; Al = 27.3; Si = 28; P = 31; S = 32; Cl = 35.5.

In these two series, elements which we recognize as similar come to stand together as Li and Na, Mg and Be, C and Si, O and S, etc. The gradual change in the properties of the members of the series, as we pass from left to right, is noticed particularly, if we consider the compounds which the elements form. Thus, only the four last members combine with hydrogen, yielding—

$$RH_4,\ RH_3,\ RH_2,\ RH.$$

The character of these hydrogen compounds also changes gradually, according to the position in the series. ClH is a marked acid of great stability, SH_2 is a weak acid decomposable by heat, PH_3 is not an acid, and is less stable than the preceding compounds, and this is still more true of SiH_4.

Considering the oxides of the members of the second series we have—

$$\begin{array}{l} Na_2O,\ Mg_2O_2,\ Al_2O_3,\ Si_2O_4,\ P_2O_5,\ S_2O_6,\ Cl_2O_7. \\ \qquad\ \text{or } MgO, \qquad\quad \text{or } SiO_2, \quad\ \text{or } SO_3, \end{array}$$

From left to right in this series the basic properties grow weaker and the acid properties stronger. Again, in the composition of the hydroxides, the same regularity is observed:—

$$Na(OH),\ Mg(OH)_2,\ Al(OH)_3,\ Si(OH)_4,\ PO(OH)_3,$$
$$SO_2(OH)_2,\ ClO_3(OH).$$

Another point to be noted is this: that, in the series with which we are dealing, the metals are at one end and the so-called non-metals at the other, while in the middle those elements come which are sometimes placed with the metals and sometimes with the non-metals, as, for instance, Si.

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* Annalen d. Ch. u. Pharm., 7 Suppl. 356.

But, just as the chemical properties undergo gradual change in the series mentioned, so also a corresponding change is noticed in the physical properties. To illustrate this, the specific gravities and the atomic volumes of the members of the second series are given:—

	Na	Mg	Al	Si	P	S	Cl
Spec. gr.	0.97	1.75	2.67	2.49	1.84	2.06	1.33
Atom. vol.	24	14	10	11	16	16	27

	Na_2O	Mg_2O_2	Al_2O_3	Si_2O_4	P_2O_5	S_2O_6	Cl_2O_7
Spec. gr.	2.8	3.7	4.0	2.6	2.7	1.9	?
Atom. vol.	22	22	25	45	55	82	?

Another series corresponding to the two already given is the following:—

	Ag = 108;	Cd = 112;	In = 113;	Sn = 118;	Sb = 122;	Te = 125 ?;	I = 127
Sp. gr.	10.5;	8.6;	7.4;	7.2;	6.7;	6.2;	4.9.

It can be shown that all the elements may be arranged in series similar to the above, and thus a very intimate connection between the atomic weights and the properties of the elements is shown to exist. It will be noticed that the changes in the properties of the elements are *periodic.* First these properties change according to the increasing atomic weights, then they are repeated *in a new period* with the same regularity as in the preceding series. Such series as those already mentioned are called *small periods.* If H is placed in the first series, then Li, etc., come in the second series, Na, etc., in the third, etc.

But all the known elements cannot be arranged in the small periods, and, what is much more important, the corresponding members of the even (4, 6, etc.) periods, or of the uneven (5, 7, etc.), resemble each other more closely than the members of the even periods resemble those of the uneven periods. This may be seen from the following example:—

Fourth period:	K,	Ca,	—	Ti,	V,	Cr,	Mn.
Fifth " :	Cu,	Zn,	—	—	As,	Se,	Br.
Sixth " :	Rb,	Sr,	—	Zr,	Nb,	Mo,	—
Seventh " :	Ag,	Cd,	In,	Sn,	Sb,	Te,	I.

The members of the fourth and sixth periods resemble each other more closely than they resemble the members of the fifth or seventh periods; and the members of the fifth and seventh periods resemble each other closely. The last members of the even periods resemble in many respects the first members of the succeeding uneven series. Thus Cr and Mn in their basic oxides are similar to Cu and Zn. On the other hand, between the last members of the uneven periods and the first members of the succeeding even periods, there are very marked differences, as, for instance, between Br and Rb. Further, between the last members of the even periods and the first members of the uneven periods, all those elements which cannot be arranged in the small periods would, according to their atomic weights and properties, naturally come. Thus between Cr and Mn, on the one hand, and Cu and Zn, on the other, Fe, Co, and Ni would come; the following series being thus formed:—

Cr = 52; Mn = 55; Fe = 56; Co = 59; Ni = 59;
Cu = 63; Zn = 65.

As Fe, Co, Ni follow the fourth period, so Ru, Rh, Pd follow the sixth period, Os, Ir, Pt follow the tenth period. Two small periods (an even and an uneven), together with an intermediate series of the elements just mentioned, form a *large period*. As the intermediate members mentioned correspond to none of the seven small periods, they form an independent eighth group:—

Fe = 56; Ni = 59; Co = 59.
Ru = 104; Rh = 104; Pd = 106.
Os = 193?; Ir = 195?; Pt = 197.

The members of this group resemble each other in the same way as the corresponding members of the even periods, as, for instance, V, Nb, Ta, or Cr, Mo, W, and others.

The two following tables of Mendelejeff show clearly the relations described. In the first, the elements with their atomic weights are arranged in large periods; in the second, they are arranged in groups and series in such a manner as to distinctly indicate the differences in the even and uneven periods.

TABLE I.

			K = 39	Rb =85	Cs =133	—	—
			Ca = 40	Sr =87	Ba =137	—	—
			—	?Yt =88?	?Di =138?	Er =178?	—
			Ti = 48?	Zr =90	Ce =140?	?La =180?	Th = 231
			V = 51	Nb =94	—	Ta =182	—
			Cr = 52	Mo =96	—	W =184	U = 240
			Mn = 55	—	—	—	—
			Fe = 56	Ru =104	—	Os =195?	—
			Co = 59	Rh =104	—	Ir =197	—
Typical elements.			Ni = 59	Pd =106	—	Pt =198?	—
H=1	Li = 7	Na = 23	Cu = 63	Ag =108	—	Au =199?	—
	Be = 9.4	Mg = 24	Zn = 65	Cd =112	—	Hg =200	—
	B = 11	Al = 27.3	—	In =113	—	Tl =204	—
	C = 12	Si = 28	—	Sn =118	—	Pb =207	—
	N = 14	P = 31	As = 75	Sb =122	—	Bi =208	—
	O = 16	S = 32	S − 78	Te =125?	—	—	—
	F = 19	Cl = 35.5	Br = 80	I =127	—	—	—

It is not necessary here to point out all the properties of the elements which can be shown to vary in harmony with the changes of the atomic weights. What has already been said will suffice to indicate the principle involved in the construction of the tables of Mendelejeff. Close study of these tables would undoubtedly show that they contain some imperfections and apparent contradictions; still, these are not numerous enough or serious enough to materially interfere with the value of the tables. It is evident that the first condition for the construction of such tables is the correct determination of all the atomic weights. We have seen with what difficulty this determination is often attended, and how doubtful some of the results obtained are. When all the atomic weights shall have been accurately determined, and when all the properties, both physical and chemical, of the elements are known, then a table constructed on the principle involved in the construction of the above tables will, in all probability, show

TABLE II.

Series.	Group I. — R_2O	Group II. — RO	Group III. — R_2O_3	Group IV. RH_4 RO_2	Group V. RH_3 R_2O_5	Group VI. RH_2 RO_3	Group VII. RH R_2O_7	Group VIII. — RO_4
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	? Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
8	Cs = 133	Ba = 137	? Di = 138	? Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	? Er = 178	? La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

a perfect accordance between atomic weights and properties. Perhaps then, too, the law of variation being known, it may be possible to propose a satisfactory theory in regard to the nature and conduct of atoms. Such a theory will be the legitimate result of the scientific chemical investigations now being carried on. The atomic theory of Dalton, as at present accepted, will eventually prove to be but a part of a more comprehensive atomic theory, which latter will be the theory of chemistry, corresponding to the theory of heat and the theory of electricity in the broad domain of physics.

Mendelejeff proposes to use the *periodic law*, as he calls the simple rule governing the variations in the atomic weights and properties of the elements in his tables, for the purpose of determining the properties of undiscovered elements. In Table II. it will be seen that, in the fourth series, a member is wanting between calcium and titanium. The atomic weight of this element would be about 44, and its properties can also be very nearly foretold from its position. It would somewhat resemble boron; its oxide would have the composition R_2O_3, and its properties would bear the same relation to Al_2O_3 that CaO bears to MgO, or TiO_2 to SiO_2; consequently it must be a more energetic base than Al_2O_3 and would resemble it in corresponding compounds. Its sulphate would not be as easily soluble as aluminium sulphate, because calcium sulphate is more difficultly soluble than magnesium sulphate. Thus, throughout the whole list of properties, such comparisons are made, and the unknown element is more accurately described than some of those which have been known for a long time.

Such speculations are, without doubt, very attractive, but we must not forget that the tables, which are used as their foundation, are more or less imperfect, and hence the conclusions drawn must necessarily be doubtful. On the other hand, the time will come when such speculations can be indulged in without risk of reaching doubtful results. The approach of this time will be hastened by just such efforts as those of Mendelejeff to discover the law governing the connection between the atomic weights and the properties of the elements.

Lothar Meyer's Arrangement of the Elements.—Another arrangement of the elements showing the connection between the atomic weights and the properties of the elements is that of Lothar Meyer, already alluded to. His table follows—

I.										
II.	B 11.0	C 11.97	N 14.01	O 15.96	F 19.1			H 1	Li 7.01	Be 9.3
III.	Al 27.3	Si 28	P 30.96	S 31.98	Cl 35.37				Na 22.99	Mg 23.94
IV.	? 47?	Ti 48	V 51.2	Cr 52.4	Mn 54.8				K 39.04	Ca 39.90
V.	? 70?	? 72?	As 74.9	Se 78	Br 79.75	Fe 55.9	Co 58.6	Ni 58.6	Cu 63.3	Zn 64.9
VI.	? 88?	Zr 90	Nb 94	Mo 95.6	? 98?				Rb 85.2	Sr 87.2
VII.	In 113.4	Sn 117.8	Sb 122	Te 128	I 126.53	Ru 103.5	Rh 104.1	Pd 106.2	Ag 107.66	Cd 111.6
VIII.	? 173?	? 178 ?	Ta 182	W 184	? 186 ?				Cs 132.7	Ba 136.8
IX.	Tl 202.7	Pb 206.4	Bi 207.5			Os 198.6	Ir 196.7	Pt 196.7	Au 196.2	Hg 199.8

This table contains all the elements whose atomic weights have been determined with any degree of certainty. The series here represented resemble those in Mendelejeff's tables. In some respects, the arrangement is more imperfect than that already considered. Meyer further points out the connection between the atomic weights and the following properties of the elements: specific gravity in the solid condition, as shown by a comparison of the atomic volumes; metallic ductility, fusibility and volatility; crystalline form; influence upon the refraction of light; specific heat; conducting power for heat and electricity. The connection is not always very clearly discernible, but careful examination and the exclusion of sources of error as far as possible show that the connection is an actual one. It remains for the future to establish the close connection which exists, but which is thus far mostly hidden.

The position of the elements in the electro-chemical series is undoubtedly dependent on the position in the series of atomic weights, but it is such an exceedingly difficult thing to determine the proper order of the members in the electro-chemical series, that the connection between the two series is not plainly recognizable.

V.

VALENCE OR ATOMICITY OF ELEMENTS.

Definition.—The means for the determination of the molecular formulas of compounds have already been considered, and it has been shown that these formulas can be determined with a considerable degree of certainty by the aid of Avogadro's hypothesis. If we now examine the formulas as determined, certain new characteristics of the elements will present themselves. Let us take a few examples among the hydrogen compounds.

I.	II.	III.	IV.
ClH,	OH_2,	NH_3,	CH_4,
BrH,	SH_2,	AsH_3,	SiH_4.
IH,	SeH_2,	SbH_3,	
FlH,	TeH_2,	PH_3,	

We see here that Cl, Br, I, and Fl each combine with H in the proportion of atom for atom; O, S, Se, and Te combine with H in the proportion of two atoms of hydrogen for one atom of the other element; in the compounds with N, As, Sb, and P, three atoms of hydrogen are in combination with one atom of the other element; and, lastly, four atoms of hydrogen are in combination with one atom of C or Si. The elements here mentioned are representatives of four great classes. If we consider the members of the first class, we shall find that the compounds which they form with each other are of the simplest kind. Indeed, they combine with each other only in one proportion, forming thus but one kind of compounds. If we take, for instance, hydrogen and chlorine and allow them to combine under the most varied conditions, the result is always hydrochloric acid, and this always contains 35.5 parts by weight of chlorine to 1 part by weight of hydrogen. The same is true of other members of the class, as bromine, potassium, sodium, etc. If, on the other hand, we consider the members of any of the other classes, we shall find that a greater variety presents itself in their combinations, not only with each other, but with the elements of the first class. Oxygen combines with hydrogen in two proportions, forming water and hydrogen peroxide; nitrogen combines with oxygen in five proportions, forming nitrous oxide, nitric oxide, nitrogen dioxide, nitrous anhydride, and nitric anhydride; carbon combines with hydrogen in a very large number of proportions, forming several series of hydrocarbons. In the foregoing, we have an indication of some property of the elements which we have not thus far considered. In studying the elements now with reference to this new property, our first duty would plainly be to study all the compounds of the elements in order to get as broad a foundation of facts as possible. We would thus finally be enabled to draw the following conclusion:—

> *Some elements combine with each other only in one proportion; others combine with each other and with other elements in more than one proportion.*

This conclusion involves no hypothesis, but is the legitimate outgrowth of the known facts. The distinction made between the two classes of elements is fundamental.

But there must be some reason for the difference. Where shall we seek for it? If we accept the atomic theory of Dalton, we must seek for the proximate causes of phenomena presented to us by masses of elements or their compounds in the atoms composing these masses. Here, then, we are to find in the atoms themselves the proximate cause of the new property of elements which we are considering. As, however, we can learn nothing of atoms directly, but only of masses of atoms, it is evident that this cause cannot be discovered, but must finally be imagined just as the atom itself is still only imagined to exist. In other words, our ideas of atoms must become enlarged in such a way as to account for the new property, or a subordinate hypothesis must be formed to supplement the atomic theory. Before forming this hypothesis let us see whether we can learn anything more in regard to the new property than we have yet learned.

We have seen above that, on examining the formulas of chemical compounds and comparing them with each other, the molecules of some of the compounds contain only one atom of hydrogen to each atom of the other element; in the molecules of other compounds we find two atoms of hydrogen to one atom of the other constituent; in others three, and in still others four atoms of hydrogen combined with one atom of some other element. In thus stating the number of atoms present in the molecules we, of course, have left the domain of facts and have already entered that of hypothesis; still, the hypothesis involved in a molecular chemical formula which has been determined by the aid of all means at our command is one which we are justified in employing, and we accordingly add the knowledge which we gain by means of this hypothesis to that which we possess from the simple study of facts, and which is represented in our conclusion above drawn. Taking into consideration the sum total of our knowledge, as thus far stated, the simplest hypothesis which it is possible to form concerning the cause which we are striving to find would be the following: Every atom of an element has an inherent power of holding in combination a certain number of other atoms, this number being dependent upon the combining power of the atoms held in combination. The simplest atoms would represent the unit of this power, and we would distinguish between these simplest or unit-atoms, and such as have the power of holding in combination two, three, four, or more unit-atoms.

Name of the New Property.—The property of the elements which we are studying has, in accordance with the simple hypothesis just given, been termed *atomicity*, *quantivalence*, or only *valence*.* The elements which consist of the unit-atoms are hence called *monatomic* or *univalent;* those consisting of atoms which have twice the combining power of the unit-atoms are called *diatomic* or *bivalent;* and in a similar manner we have *triatomic* or *trivalent*, *tetratomic* or *quadrivalent*, etc. elements. Further, the elements are called respectively *monads*, *dyads*, *triads*, *tetrads*, *pentads*, *hexads*, etc. Accordingly, of the elements in the brief table, given at the beginning of this article (p. 79), all those in the first line are univalent; oxygen, sulphur, selenium, and tellurium are bivalent; nitrogen, arsenic, antimony, and phosphorus are trivalent; and carbon and silicon are quadrivalent. Quadrivalent.

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* In regard to the choice between the three expressions given, it may be said that the word valence seems to be less objectionable than the others which have been used, because it is the simplest and, at the same time, it expresses all that we desire to express with reference to the property which it designates. Again, the word atomicity has been used in another sense, and hence its use might lead to confusion, some authors employing it in its first sense, others in the new and entirely different sense. By a monatomic, diatomic, etc. element is sometimes meant an element whose molecule consists of one, two, etc. atoms. As it is necessary to have words to express this latter sense, it seems

Distinction between Valence and Affinity.—The property of valence must not be confounded with that of affinity. By affinity is usually meant the force with which one atom attracts another or others. Valence has apparently no connection with this force. An element may, in general terms, have a strong affinity for other elements, and yet be univalent. Another may possess but a weak affinity and be quadrivalent. Thus, chlorine has a strong affinity for hydrogen, the two combine with great energy, yet they are both univalent elements. While carbon does not combine with chlorine with nearly as great energy as hydrogen does, it nevertheless is quadrivalent; its atom is capable of holding in combination four atoms of hydrogen. The two properties, valence and affinity, are possessed by every atom and exhibit themselves every time that atoms act upon each other, the latter determining the energy of the action, the former, the complexity of the resulting molecule.

Methods for determining the Valence of the Elements.—The foundations upon which the conception of valence rests, and the conception itself being thus explained, let us inquire how we can determine the valence of the individual elements. We have recognized certain cha-

desirable to leave the word atomicity and its adjective-derivatives, monatomic, diatomic, etc., to serve this purpose, while we adopt the expression valence with the derivatives univalent, bivalent, trivalent, etc., for the purpose of designating the property under discussion.

racteristics of the so-called univalent elements, and have seen that hydrogen belongs to this class. If then we are certain that hydrogen is univalent, we may employ it as a means of measuring the valence of other elements. The first general rules to guide us in the measurements would be—

1. Those elements which combine with hydrogen in the proportion of 1 atom to 1 atom are univalent. Such, for instance, are chlorine, bromine, etc. F[illegible] Li K Ag

2. Those elements which combine with hydrogen in the proportion of 1 atom to 2 atoms of hydrogen are bivalent. Such, for instance, are oxygen, sulphur, etc. Ca Ba

3. Those elements which combine with hydrogen in the proportion of 1 atom to 3 atoms of hydrogen are trivalent. Such, for instance, are nitrogen, phosphorus, etc. Sb. As

4. Those elements which combine with hydrogen in the proportion of 1 atom to 4 atoms of hydrogen are quadrivalent. Such, for instance, are carbon, silicon, etc. Sn Ci

But only comparatively a small number of the elements combine with hydrogen alone, so that this method must necessarily be of limited application. It is plain, however, that, if our conception of valence, as above explained, is correct, it is not necessary that we should employ hydrogen as our standard in measuring it. Any other univalent element may answer the same purpose. Having then first determined by means of hydrogen that chlorine and bromine are univalent, we may employ either of these as standards in the same manner as we employed hydrogen above. This would enable us to extend our measurements much further, and, eventually, to take in all the elements. In all cases in which the molecular formulas of the chlorine or hydrogen compounds of the elements can be determined according to the principles of Avogadro's hypothesis, the determination of the valence is, according to the rules given, a simple matter.

To illustrate the application of the method, let us take an example. Suppose we wish to determine the valence of oxygen. Oxygen forms two compounds with hydrogen. H_2O + H We analyze both of these compounds, and find that water contains the smallest proportion of oxygen to hydrogen. We assume, therefore, that in the molecule of water there is but one atom of oxygen; and we consequently take this compound for the purpose of making our determination. The molecular weight is found to be 18; and this, taken in conjunction with the results of the analyses, shows us that 16 parts of oxygen are combined with 2 parts of hydrogen. The atomic weight of hydrogen is already known to be 1. Hence one atom of oxygen is combined with two atoms of hydrogen; and hence, further, oxygen is a bivalent element.

Insufficiency of the Hypothesis.—In attempting to subdivide the elements into classes according to their valence, difficulties are met with; and these are so great that the hypothesis as already given proves inadequate, and must undergo change in order to be in harmony with the facts. The conception of valence with which we have been dealing is the simplest which is held. It is, too, the first form in which it was brought to light. For these reasons it has been explained in full. It is now necessary, however, to show in what respects it is inadequate, and to show what changes it has undergone.

The original form of our hypothesis, as above stated, was: Every atom has an inherent power of holding in combination a certain number of other atoms, this number being dependent upon the combining power of the atoms held in combination.

According to this, phosphorus, which combines with hydrogen, forming the compound PH_3, ought, in combining with chlorine, to form the compound PCl_3, and there stop. Nitrogen, which forms the compound NH_3, ought to show itself as a trivalent element wherever it is met with. In the case of phosphorus, however, we have not only the chlorine compound PCl_3, but another, PCl_5; in the case of nitrogen, too, we have not only a whole series of compounds in which it plays the part of a trivalent element, but also a very large series in which it just as surely plays the part of a quinquivalent element. Thus we have, on the one hand, ammonia, NH_3, hydroxylamine, $\overset{III}{N}\overset{II}{H_2}(\overset{I}{OH})$, nitrous acid, $\overset{III}{N}\overset{II}{O}(\overset{I}{OH})$, etc., in which nitrogen is trivalent; while, on the other hand, we have ammonium chloride, $\overset{V}{N}\overset{IV}{H_4}\overset{I}{Cl}$, nitric acid, $\overset{V}{N}\overset{IV}{O_2}(\overset{I}{OH})$, and the whole list of nitrates and ammonium salts in

omit

which nitrogen is quinquivalent. A number of other instances could be given, showing that one and the same element exhibits different combining powers in different compounds, so that, if we attempted to classify the elements according to the valence, we would place the same element now with the trivalent and now with the quinquivalent; another would find its place with the bivalent and again with the quadrivalent, according as one or another compound of these elements is taken as the means of judging of the valence. Plainly, then, the conception of valence needs enlargement, for, as above stated, it has not a true foundation of facts.

Atomic and Molecular Compounds.—The difficulty just indicated was early recognized, and an attempt was made to surmount it by introducing another hypothesis in regard to the nature of chemical compounds. According to this new hypothesis, there are two kinds of chemical compounds, which are called *atomic* and *molecular*. In the former of these, we have the true chemical compounds, in the sense in which we have understood that expression from the beginning. In these, the atoms exhibit all the properties which we have thus far recognized as belonging to them—including valence. By virtue of these properties, the compounds have their existence. In the molecular compounds, on the other hand, a new force is supposed to act, this force being distinct from the interatomic force, and acting in a peculiar way between molecules. The molecules are supposed to be first formed by means of chemism, etc., and, when these have been formed, all that can be effected by valence has been effected. But now it is further supposed that the molecules thus formed have an attractive power and combining power of their own, by virtue of which the molecular compounds are formed. The most common examples of molecular compounds are salts containing water of crystallization. These are formed by virtue of the attraction of the molecules of the salt for the molecules of the water. But, according to the propounder of this hypothesis, we have further examples of molecular compounds in phosphorus chloride, PCl_5, and in ammonium chloride, NH_4Cl. In the former of these, a molecule of PCl_3, a true atomic compound, holds in combination a molecule of chlorine (Cl_2), also an atomic compound. In the latter, a molecule of NH_3, an atomic compound, holds in combination a molecule of hydrochloric acid, also an atomic compound.

Foundation for the Distinction between Atomic and Molecular Compounds.—Of course, in order that such an hypothesis as that under consideration should be at all permissible, it must be shown that there are differences between those compounds which are called molecular and those which are called atomic. To a certain extent this is possible. In the case of salts containing water of crystallization, there can, at least usually, be no difficulty in recognizing that the force holding together the salt and the water is of a different nature from that which holds the constituents of the salt together, or that which holds the constituents of the water together. It is only necessary to heat the compounds gently in order to overcome the attraction and cause the breaking up of the complex molecule; in some cases, indeed, the attraction is so weak that it is only necessary to expose the compound to the air, when the water passes off in the form of vapor, leaving the molecules of the salt intact. This weakness of the union is then a principal characteristic of molecular combination.

Now, if we examine the compounds above referred to, viz., PCl_5 and NH_4Cl, we find that they possess this characteristic. It has been shown, when considering the cases of anomalous specific gravities of vapors, that, when PCl_5 and NH_4Cl are heated to a sufficient degree to convert them into vapor, they are broken up into PCl_3 and Cl_2, and NH_3 and HCl, just as the crystallized salts lose their water of crystallization by being heated. So, also, in a number of other cases, it can be shown to be true that compounds, which we must consider as molecular in order to explain their existence and yet retain the hypothesis of valence, as above stated, break up under the influence of heat into simpler molecules.

We thus see that there is some foundation for assuming the existence of molecular compounds as distinct from atomic compounds. But how does this help us in surmounting the difficulty already met with in attempting to apply the principle of the hypothesis of valence for the purpose of classifying the elements?

Use of the Distinction.—It is plain that atomic compounds would be the only ones which we could employ for the purpose of determining the valence of atoms. Thus, the only chlorine compound of phosphorus which we could employ for the purpose of determining the valence of phosphorus is PCl_3. The other compound, PCl_5, the existence of which would seem to indicate that phosphorus is quinquivalent as well as trivalent, being a molecular compound, is formed independent of the valence of phosphorus and does not at all interfere with the acceptance of the original hypothesis of valence. So, too, in all similar cases. Nitrogen is really trivalent, but, owing to the formation of molecular compounds, it appears oftentimes to be quinquivalent. By a generous application of this principle, there is no difficulty in accounting for the anomalous cases, and our hypothesis of valence may still be retained, unless it can be shown that there are facts, not yet considered, which do not harmonize with it.

Difficulties met with.—One difficulty immediately presents itself. Although the examples above given show that there are compounds which seem to differ from true chemical compounds to a sufficient extent to justify us in assuming that they belong to another class of compounds, still, there are cases in which there is no ground whatever for making this assumption, and which, nevertheless, show plainly that one and the same element may be at one time trivalent, at another quinquivalent, unless we make the above assumption without ground. The compound $POCl_3$, for instance, is not decomposed when converted into the form of vapor, and we have just as much right to consider it a true chemical compound as we have to consider PCl_3 as such. But, in $P\overset{\prime\prime}{O}\overset{\prime\prime\prime}{Cl}_3$, phosphorus is quinquivalent, while in PCl_3 it is trivalent. Evidently, here our only ground for considering $POCl_3$ a molecular compound is the fact that its existence cannot be explained by the original hypothesis of valence. This is dangerous reasoning, and, if we follow it, we shall soon be in serious difficulties. We saw above that all the nitrates and ammonium salts can only be explained on the supposition that the nitrogen in them is quinquivalent, unless we suppose them to be molecular compounds. Plainly, it would be next to absurd to indulge in the latter supposition, as both the nitrates and the ammonium salts have all the characteristics of true chemical compounds, and, if we can assume that they are only molecular compounds, in order to suit our purpose, then we are at liberty to make the same assumption in regard to almost any compound in the field of chemistry.

Experiments showing that Nitrogen may be both Trivalent and Quinquivalent.—Again, an experiment has been recently performed which appears to show that ammonium chloride, NH_4Cl, and analogous compounds of nitrogen, are true atomic compounds. If NH_4Cl is a molecular compound, then, as was explained above, two forces are concerned in the formation of its molecule.

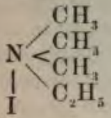
1st. A force holding together the nitrogen atom and three hydrogen atoms forming the molecule NH_3; and the hydrogen atom and chlorine atom forming the molecule HCl.

2d. A force holding together the molecule NH_3 and the molecule HCl.

If these two forces are distinct in character, the resulting molecule might be represented by the formula $(NH_3 + HCl)$. Suppose now we add together two other molecules such that, taken together, they are the same in number and quantity with those contained in the compound $(NH_3 + HCl)$. Then the resulting compound ought not to be identical with that obtained in the former case. If these new molecules are, for instance, NH_2Cl and H_2, then the compound will be $(NH_2Cl + HH)$ and this should not be identical with $(NH_3 + HCl)$, although its composition is exactly the same.

This principle has been tested, not, indeed, with the molecules employed in the above explanation, but with others analogous to them. Instead of NH_3, the analogous compound, $N(CH_3)_3$, was taken and this was united with $(C_2H_5)I$. Thus, a compound was obtained which, if it be molecular, may be represented by the formula $(N(CH_3)_3 + C_2H_5I)$. Again the compound $N(CH_3)_2C_2H_5$ was taken, and this was united with CH_3I, yielding a compound which, as in the former case, may be represented by the formula $(N(CH_3)_2C_2H_5 + (CH_3)I)$. Now, these two new compounds ought not to be identical, if they are molecular and not atomic. On comparing them, however, they were found to be in every respect identical.

From this experiment it is concluded that the compounds studied are atomic compounds, and that in them nitrogen is quinquivalent. Each group (CH_3), (C_2H_5), and the element I being held by the same kind of force, the identity of the resulting compounds is readily understood. We have in each—



$$\underset{\displaystyle I}{\underset{|}{N}} \left< \begin{matrix} CH_3 \\ CH_3 \\ CH_3 \\ C_2H_5 \end{matrix} \right.$$

As was stated in a previous chapter, the compound PCl_5 can be converted into the form of vapor under certain circumstances, viz., in the presence of the vapor PCl_3. From this it is concluded that the compound PCl_5 is a true chemical or atomic compound; and hence, further, that the phosphorus atom contained in it is quinquivalent.

The Distinction between Atomic and Molecular Compounds unnecessary as far as the Hypothesis of Valence is concerned.—We recognize thus that nitrogen and phosphorus act in some compounds as trivalent, in other compounds as quinquivalent, elements. If we acknowledge this, however, then there is no necessity for assuming the existence of molecular compounds for the purpose of explaining anomalies in the valence of elements. It is very probable, indeed, that, in the so-called double compounds in which we have two or more salts combined with each other, as well as in the salts containing water of crystallization, we have true examples of molecular compounds, in the sense in which this expression has been used in the present article; but it is evident that, as soon as we admit the possibility of one and the same element being either univalent or bivalent, it is no longer necessary to assume the existence of these molecular compounds. We hence leave the study of these peculiar and interesting compounds for the future, and continue our discussion of valence.

Saturated and Unsaturated Compounds.—As soon as the quinquivalence of nitrogen was established, a new explanation was offered concerning the nature of nitrogen compounds. Only those compounds in which the nitrogen is quinquivalent were looked upon as complete. Those in which the nitrogen is trivalent were looked upon as incomplete. For the expressions complete and incomplete, the expressions saturated and unsaturated were employed. The atom of nitrogen having the power to hold in combination five univalent elements or groups is *saturated* when all of its powers are employed, as in the compound NH_4Cl; it is *unsaturated* when only a part of its powers are employed, as in the compound NH_3. The power of the nitrogen atom was expressed by saying that it possesses five *affinities.* In the saturated compound all of these affinities are employed, whereas in the unsaturated compound only a part of them are employed.

To explain the fact that ammonium chloride, NH_4Cl, is readily decomposed by heat, yielding NH_3 and HCl, it was further supposed that of the five affinities of the nitrogen atom two are weaker than the other three. Hence, in a saturated nitrogen compound, two atoms or groups are held less strongly than the other three, and are given off more readily. This same explanation would account for the decomposition of phosphorus chloride, PCl_5, into PCl_3 and Cl_2, and the other similar decompositions to which reference has already been made. The experiment described above, however, which proved the identity of the compounds—$(N(CH_3)_3 + C_2H_5I)$ and $N(CH_3)_2(C_2H_5) + CH_3I$—proved also that the affinities of the nitrogen atom are all of the same kind, and hence we cannot admit that two of the affinities are weaker than the other three. While, further, phosphorus chloride, PCl_5, is readily decomposed by heat, in accordance with the supposition that two of the affinities of the phosphorus atom are weaker than the other three, yet, on the other hand, the compound $POCl_3$ gives no evidence of this difference of the affinities. It can also easily be shown that it is not necessary to assume this difference in order to explain the decomposition of phosphorus chloride, PCl_5, and ammonium chloride, NH_4Cl. We may, for instance, suppose that the five affinities of the nitrogen atom, or the phosphorus atom, are all exactly equal in power at the outset. Should three of these affinities, however, become saturated, it seems possible that the presence of the saturating atoms or groups may influence the power of the remaining unsaturated affinities in such a way as to make them weaker than they were at first.

With the evidence before us, it seems that we are justified in abandoning the view that the affinities of the nitrogen atom and similar pentavalent atoms differ from each other in the strength of the attraction which they exert towards other atoms. It remains then yet to explain, by the aid of some other hypothesis, the ready decomposition of ammonium chloride and phosphorus chloride.

Double Union.—To account for the existence of unsaturated compounds, some chemists have supposed that two affinities of the same atom might in some way act upon each other, causing saturation. The compound in which such a combination exists would then be a complete compound, not possessing free affinities. In them, however, the mutual saturation of like affinities could be easily overcome, and then other atoms could be held in combination. This was supposed to be rendered probable by the fact that the number of affinities which are considered as free in unsaturated compounds is always, with very few exceptions, an even number. This would necessarily be the case if the above assumption were true. The idea of double union has undoubtedly been of service in some cases, as, for instance, in the theory of the so-called aromatic compounds; but it remains still to be shown whether there is a sufficient basis of facts for it to rest upon.

Variable Valence.—We have already seen that nitrogen and phosphorus act in some compounds as though they were trivalent; in others, as though they were quinquivalent. On examining the compounds of other elements, as we have examinnd those of nitrogen and phosphorus, we should find that some of these also appear at times to have one valence, and at other times another valence. As a consequence of such observations, the hypothesis of valence as first stated in its simplest form was changed, and the change has been accepted by some. Instead of supposing the valence of an atom to be a constant property determined by the nature of the atom, just as the weight and many other properties are necessarily connected with the atom and are constant, it was supposed that the valence could change according to circumstances. These circumstances might be of various kinds, but prominent among them was the temperature. Accordingly, in some of their compounds, nitrogen and phosphorus are trivalent, and in others quinquivalent. Inasmuch as the ammonium compounds, in which the nitrogen is quinquivalent, are decomposed by heat, yielding ammonia, in which the nitrogen is trivalent, and as, further, phosphorus chloride, in which the phosphorus is quinquivalent, is decomposed by heat, yielding phosphorus trichloride, in which the phosphorus is trivalent, the conclusion was drawn that, at lower temperatures, the valence of these elements is greater, and that the valence decreases with an increase of temperature.

The change thus made in the hypothesis of valence has led to a much more comprehensive change affecting the valence of every element. Not only could the valence of some few elements vary according to circumstances, but now the valence of all elements is variable. The same element may be univalent, trivalent, quinquivalent, heptavalent, etc. Another may be bivalent, quadrivalent, hexavalent, etc. All the elements are divided into two classes, called *artiads* and *perissads*. The members of the former class may have any valence represented by an even number, as 2, 4, 6, 8, etc. Those of the latter class may have any valence represented by an uneven number as 1, 3, 5, 7, etc. There is, to be sure, a prevailing tendency on the part of each element to act with some particular valence, but, nevertheless, as occasion demands, new powers may be called into requisition, or some of those which usually exhibit themselves may disappear.

Objections to the Idea of Variable Valence.—The objection which we have to this view is the following: We conceive the valence of an element to be a very important property. Hence, the difference between univalence, trivalence, and quinquivalence is a great difference, and the change from one to the other is a great and important change. To say that an atom has now the power of holding in combination only one univalent atom, and that, in so doing, all its power is employed; and, again, to say that the *same* atom has three, five, or even seven times this power, presupposes very peculiar notions concerning the nature of force. Where shall we find any analogy for this startling kind of metamorphosis? This power of the atoms, it must be remembered, is actual power, it is tangible, it is a form of energy.* Do, then, the atoms originate and annihilate energy at will? Can they multiply or divide the energy which they possess in one compound by five or seven, so as to be correspondingly stronger or weaker in another compound? If we accept this view, we must ascribe to the atoms themselves creative power and the power to annihilate energy. This we prefer not to do, and hence, we do not accept the hypothesis of variable valence, in the sense in which that expression has been used in this article.

Würtz's View.— Würtz has recently employed the term valence in a sense differing entirely from that in which we have thus far understood it, and in which it has been used by most writers. By it he means the power which an atom actually exhibits in any given compound, not the absolute power of the atom to hold other atoms in combination. He says: "We think that the important thing is not to fix the atomicity which each element possesses absolutely, but that which it manifests in a given compound." He then points out the difficulties in the way of determining the absolute atomicity of an element, and abandons the attempt to accomplish the determinations. Further, he calls attention to the fact that the force with which one atom attracts another depends upon the properties of both atoms, and cannot be measured absolutely by the force of one of the atoms. So also, he conceives that an atom may be trivalent towards one kind of atoms and quinquivalent towards another. He says, in this connection: "The property which phosphorus possesses of uniting with five atoms of chlorine depends, without doubt, upon a particular condition of the atoms, their form, structure, volume, movements. This condition, which is unknown to us, is invariable for phosphorus, and if one atom of phosphorus can attract five atoms of chlorine, while it can only unite with three atoms of hydrogen; if it is quinquivalent as regards chlorine, and trivalent as regards hydrogen, we ought to seek for the reason of these differences, not only in the atoms of phosphorus, but also further in those of chlorine and of hydrogen."

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* The potential energy of a free atom must be dependent upon two things, viz., the affinity of the atom for other atoms, and the valence of the atom, determining the number of atoms which are attracted by means of the affinity.

The proposition, then, is to throw aside the idea of valence, as it has been defined, and to substitute for it a variable idea. The valence of an atom is thus not a fixed property of the atom determining the nature of the compound which this atom forms with others, but, these compounds having been formed by virtue of unknown properties of atoms, the valence is that particular combining power which the atom happens to exhibit. The difference between these two conceptions of valence are as great as that between the conception of atomic weight and equivalent. It will be remembered that, owing to the difficulties at first encountered in determining atomic weights, it was proposed to substitute the equivalent for the atomic weight, and that the atomic weight was, for a time, abandoned. The subsequent development of the science showed that this step was a backward step, and that the first conception of Dalton of the atomic weight was the true one. Equivalents have, in turn, been abandoned, and the definite atomic weights have again taken their place.

We believe that the proposition of Würtz to abandon the definite idea of valence is analogous to the original proposition of Wollaston to abandon the definite idea of the atomic weight. There are undoubtedly strong reasons for the step proposed by Würtz, as there was for the step proposed by Wollaston. The difficulties in the way of determining the absolute valence of an element are fully as great as they are represented to be by Würtz. Nevertheless we are not prepared to follow his suggestion to abandon the definite idea of valence. We believe this valence to be a fixed and important property of every atom, the study of which will in time lead to valuable results. When investigation shall have proceeded far enough to enable us better to understand this property than we do at present, we shall probably find, as we have held throughout this discussion, that the valence of the atom determines in every case the complexity of the molecule; and that, knowing the valence and nature of the atoms entering into combination, we shall be able to foretell the composition of the molecule. Because we cannot do this at present, shall we abandon the idea completely? We do not think it advisable to do so. That which Würtz calls atomicity we would call *apparent valence*, thus distinguishing it from the *true valence.* The distinction having thus been made, let us point out more clearly the differences between apparent and true valence.

True Valence.—This has already been defined. By true valence is meant that property of an atom by virtue of which it has the power to hold in combination a certain number of other atoms. It is an invariable property for the same atom under the same conditions. It may be exerted to the full extent in a given compound, or may not be. According as it is, or is not, thus exerted to the full extent, the compounds which it forms are saturated or unsaturated. In an unsaturated compound there are free affinities, but these are not as strong as the affinities of the free atom, for these must change with the entrance into a molecule of new atoms. For instance, the affinities of an atom of phosphorus are at first equal in strength, and in every other respect. But, as soon as a part of these affinities are employed in holding atoms in place, it seems very probable that the presence of these new atoms would influence the nature of the whole molecule; and, if there are any unemployed affinities present, these too would differ from the unemployed affinities of the free atom. In some instances, this influence may be comparatively strong, and the unemployed affinities may thus be rendered very weak, so weak, indeed, that they are hardly recognizable. In other instances, this influence may be less marked, and then we would have more active unsaturated bodies, that is to say, such as would readily take up additional atoms.

Methods for determining True Valence.—In regard to the means at our command for measuring the valence of elements, we must confess to great weakness. It is impossible at present to measure the true valence of all elements with any degree of accuracy. We adopted hydrogen above as the standard for making the measurements. It still seems to us proper to do so. It does not follow, however, that the results obtained through the aid of the hydrogen compounds are necessarily the true ones. In determining atomic weights, we do not only take into consideration one particular set of compounds, but all compounds of an element, and then adopt for the determination that particular compound which contains the smallest proportion of the element. So, in determining the valence, it is right to take into consideration all the compounds of an element, and then to adopt that one which contains the largest proportion of the measuring element.

We believe, further, that there are other elements, besides hydrogen, and other atomic groups which are univalent in the same way that hydrogen is univalent. Such, for instance, are chlorine and bromine, methyl (CH_3) and ethyl (C_2H_5). These elements and groups may be used for the purpose of determining the valence of other elements, just as hydrogen is used. It may be that the results obtained by means of them may differ from those obtained by means of hydrogen. This is not necessarily fatal to the method, though such a disagreement of results might incline us to think, as Würtz thinks, that the valence of an element is not only dependent on the nature of its own atoms, but also upon the nature of the atoms with which it is combined. If this supposition of Würtz is correct, however, if, as he says, phosphorus is quinquivalent towards chlorine, how can we explain the existence of the compound PCl_3 without supposing it to be an unsaturated compound? What difference shall we understand to exist between PH_3 and PCl_3?

Apparent Valence.—The apparent valence of an element is that which Würtz calls the atomicity. It may or may not be identical with the true valence. In every compound in which the apparent valence of an element is not its true valence, there are free affinities. These may or may not be masked through the influence of the atoms or groups already present in the molecule. In many cases, the apparent valence of an element in any given compound will be determined as soon as the formula of the compound is determined. In cases where it is possible to ascribe to an element more than one valence, it is better to select the prevailing valence which it exhibits in its other compounds, unless there are good reasons for selecting some other. We ought always, however, to take the simplest view permissible.

With the conception of apparent valence just explained, and with the limitations recommended, it will be found that no element exhibits more than two different powers of combination, the majority, only one. It seems probable that in those cases in which an element exhibits only one valence, this may be the true valence. Whether this be so, is a question still to be answered. Our knowledge of true valence is so limited that, for the present, we propose to call the valence observed the apparent valence, leaving the proper development of the subject of true valence for the future.

Conclusions.—As a result of the above discussion we are prepared to make the following statements, which we believe to be in accordance with the facts, and the simplest which can be made in the present state of our knowledge.

I. Valence is a fixed property of elements, which may be fully exerted or not.

II. We do not possess satisfactory means for determining the true valence of elements.

III. We can determine the apparent valence of elements.

IV. The apparent valence may vary within narrow limits, but rarely, if ever, does one element exhibit more than two powers.

In the following table the apparent valence of each element, as determined by a variety of observations, is indicated:—

I. *Univalent Elements.*

Hydrogen,	H
Chlorine,	Cl
Bromine,	Br
Iodine,	I
Fluorine,	Fl
Potassium,	K
Sodium,	Na
Cæsium,	Cs
Rubidium,	Rb
Lithium,	Li
Silver,	Ag

II. *Bivalent Elements.*

Oxygen,	O
Sulphur,	S
Selenium,	Se
Tellurium,	Te
Barium,	Ba
Strontium,	Sr
Calcium,	Ca
Magnesium,	Mg
Beryllium,	Be
Zinc,	Zn
Cadmium,	Cd
Copper,	Cu
Mercury,	Hg
Yttrium,	Y
Erbium,	Er
Cerium,	Ce
Lanthanium,	La
Didymium,	Di

III. *Trivalent Elements.*

Boron,	B
Bismuth,	Bi
Gold,	Au
Indium,	In

IV. *Bi- and Trivalent Elements.*

Nickel,	Ni
Cobalt,	Co
Iron,	Fe
Manganese,	Mn
Chromium,	Cr
Aluminum,	Al
Uranium,	U

V. *Bi- and Quadrivalent Elements.*

Carbon,	C
Tin,	Sn
Lead,	Pb
Platinum,	Pt
Iridium,	Ir
Palladium,	Pd
Osmium,	Os
Rhodium,	Rh
Ruthenium,	Ru

VI. *Quadrivalent Elements.*

Silicon,	Si
Titanium,	Ti
Zirconium,	Zr
Thorium,	Th

The above table is, no doubt, exceedingly imperfect. Investigations, at present being carried on, are tending to perfect it. Through a knowledge of the apparent valence of elements, we shall eventually arrive at a knowledge of the true valence, and hence we attach importance to the study of this peculiar property. We are far from understanding it, so that any discussion of it must necessarily be very imperfect. In the above, the attempt has been made to show exactly where we stand with reference to this property, to show that some of the hypotheses which have been proposed corcerning this property have not foundation enough to warrant us in accepting them, and to reduce the hypotheses back to the simplest form. This is all we can do at present, and with this we close our discussion.

PART SECOND.

CONSTITUTION OR STRUCTURE OF CHEMICAL COMPOUNDS.

I.

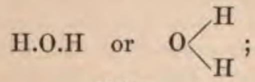
GENERAL CONSIDERATIONS.

Definition of Constitution, etc.

Definition, etc.—In considering the subject of valence, we stated that chemical compounds are formed by virtue of the mutual attraction of the free affinities of atoms upon each other; that the valence of atoms determines the complexity of the molecules into which they enter. When the compounds have once been formed, the affinities called into action are no longer free; they are saturated. Upon this mutual neutralization or saturation of free affinities are based our ideas in regard to the constitution or structure of chemical compounds. The simplest illustrations of chemical constitution are found, of course, among the compounds which univalent elements form with each other. Whatever conceptions we hold in regard to the constitution of these simplest compounds, we must, in general, hold the same conceptions in regard to the constitution of the most complicated compounds. Let us then briefly consider one simple compound, and explain definitely what we mean by its constitution.

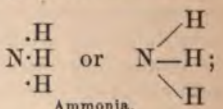
An atom of hydrogen in a free condition is a particle of matter having definite weight. This particle of matter has the power of attracting and combining with other atoms. Further, the number of other atoms which it can hold in combination is limited to *one* of the simplest kind, as, for instance, one atom of hydrogen. Now, if two atoms of hydrogen be brought in contact with each other, the powers which they possess are called into play, and, as a consequence, the two unite. As soon as the union has taken place, the powers cease to be free, they are performing their appropriate functions. In the place of the atoms, we have now a molecule of hydrogen which has not of itself any direct attractive power, enabling it directly to form chemical compounds. We are not able to state in what manner the free affinities of the two hydrogen atoms have satisfied each other. It is not at all likely, however, that a firm union between the two atoms takes place, in such a way as to render the parts of the molecule immovable with reference to each other. Much more likely is it that, after the union, the atoms perform some kind of motion with reference to each other, according to the laws of atomic motion yet to be discovered. For our present purpose, it is sufficient to know that, in whatever manner the union takes place, the chemical activity of the atoms ceases in consequence. The union then may be represented by the formula H.H, or by H—H; the point, in the one case, and the line, in the other, merely indicating the fact of union, without explaining the manner of the union. By the constitution of the molecule of hydrogen, then, we mean the arrangement of the atoms in it. Not the actual arrangement of these atoms in space, for in regard to this we know absolutely nothing.

In general terms, then, by the constitution of a molecule, we mean the arrangement of the atoms composing it. We have determined the constitution of a chemical compound when we have determined which atoms are united with each other in its molecule. We express the constitution by means of a graphic formula, indicating the union of the atoms present, as, for instance, the following are constitutional or graphic formulas:—



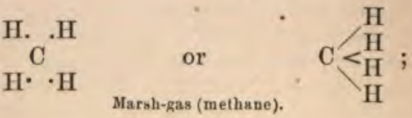
$H.O.H$ or $O\begin{matrix}\diagup H\\ \diagdown H\end{matrix}$;

Water.



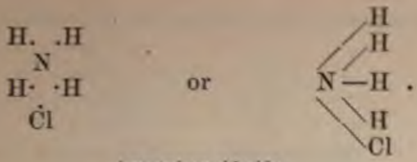
$N\begin{matrix}.H\\ \cdot H\\ \cdot H\end{matrix}$ or $N\begin{matrix}\diagup H\\ —H\\ \diagdown H\end{matrix}$;

Ammonia.



$\begin{matrix}H. & .H\\ & C & \\ H\cdot & \cdot H\end{matrix}$ or $C<\begin{matrix}H\\ H\\ H\\ H\end{matrix}$;

Marsh-gas (methane).



Ammonium chloride.

Possible forms of Combination.—The simplest forms of combination found among the elements are those in which one univalent element is combined with another univalent element. We have instances of this kind of combination in the molecules of the univalent elements themselves, as H—H, Cl—Cl, etc.; and, further, in such compounds as the following:—

H—Cl,	H—Br,	K—Cl,	NaBr,	etc.
Hydrochloric acid.	Hydrobromic acid.	Potassium chloride.	Sodium bromide.	

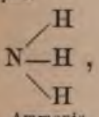
We next have those compounds in which one bivalent is combined with two univalent elements, as, for instance:—

H—O—H,	K—O—H,	Cl—O—H,	Na—O—Na, etc.
Water.	Potassium hydroxide.	Hypochlorous acid.	Sodium oxide.

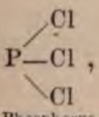
One bivalent may be united with one other bivalent element, as in the following:—

Ba=O,	Ca=O,	Mg=O,	etc.
Barium oxide.	Calcium oxide.	Magnesium oxide.	

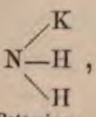
One triad may be in combination with three monads, as:—



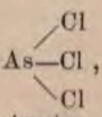
Ammonia.



Phosphorus chloride.



Potassium amide.



Arsenious chloride.

etc.

One triad may be in combination with one dyad and a monad:—

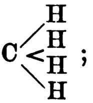
? $\text{Fe}\begin{matrix}=O\\-H\end{matrix}$

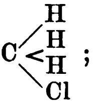
One triad may be combined with one triad:—

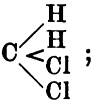
$B\equiv N$; etc.

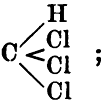
Nitrogen-boron.

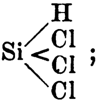
One tetrad may be combined with four monads:—

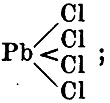

Methane.


Monochlormethane.


Dichlormethane.

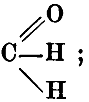

Trichlormethane.

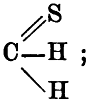

Silicon-chloroform.


Lead chloride.

etc.

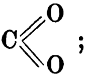
One tetrad may be combined with one dyad and two monads:—

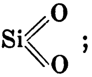

Formic aldehyde.

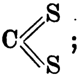

Thioformic aldehyde.

etc.

One tetrad may be combined with two dyads:—

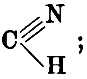

Carbon dioxide


Silicon dioxide.


Carbon disulphide.

etc.

One tetrad may be combined with one triad and one monad:—


Hydrocyanic acid.

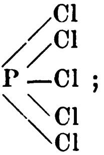
etc.

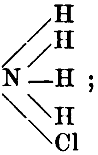
One tetrad may be combined with another tetrad:—

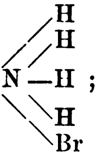
$C\equiv C$.

Probably the molecule of carbon.

One pentad may be combined with five monads:—

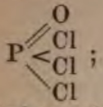
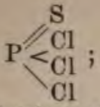
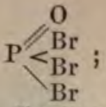

Phosphorus chloride.


Ammonium chloride.


Ammonium bromide.

etc.

One pentad may be combined with one dyad and three monads:—




etc.

Phosphorus oxichloride. Phosphorus sulphochloride. Phosphorus oxibromide.

One pentad may be combined with two dyads and one monad:—

?

One pentad may be combined with one triad and two monads:—

?

One pentad may be combined with one triad and one dyad:—

?

One pentad may be combined with one tetrad and one monad:—

?

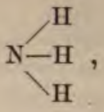
In regard to the four cases last mentioned, it will be noticed that no examples are given. No combinations of these kinds are really known. As far as we know, however, they are theoretically possible, and perhaps, in the future, we may make their acquaintance.

Types.—In the above examples we have illustrated all the principal fundamental forms of combination. The common characteristic of all these forms is this, that in each all the elements of lower valence are in combination with one element, this latter being, as it were, the typical element of the molecule. Now, all those compounds in which a monad is the typical element resemble each other closely; those in which a dyad is the typical element also resemble each other closely, and so through the list. Thus, we have the compounds divided into classes according as a monad, dyad, triad, tetrad, or pentad is the typical element. In each class we can select some one compound which is the type of the class. It is the type in the sense that the kind of combination found in it is found repeated in all the members of the class. We may thus select the five following types:—

I. $H—H$, Hydrogen.

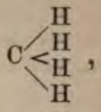
II. $H—O—H$, Water.

III.



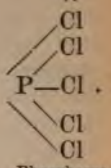
Ammonia.

IV.

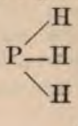
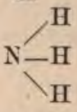


Methane.

V.

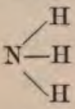
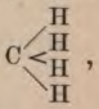
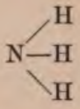
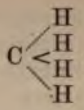


Phosphorus chloride.

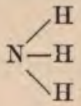
Now, by imagining the constituents of these types replaced by other atoms of equal valence, we can obtain all the examples above given, and a very large number in addition. Thus, $H—Cl$ may be looked upon as derived from $H—H$ by the replacement of one atom of H by Cl, an atom of equal valence. So, also, $Ca═O$ may be looked upon as derived from $H—O—H$ by the replacement of two atoms of H by one atom of Ca, the valence of which is equal to that of two atoms of H. Or, the typical element itself may be replaced by another of equal valence, as, for instance, in , which may be looked upon as derived from the type  by the replacement of the triad N by the triad P. It is thus clear what relation the types bear to similar compounds.

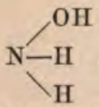
When the so-called "theory of types" was proposed, a great deal of importance was attached to it. The true secret of chemical combination was supposed to have been discovered. Efforts were made to refer every known compound to some one of the types and thus to classify the compounds. These efforts were undoubtedly valuable. They were the necessary precursors of our present views concerning the nature of chemical compounds. Through the theory of types we arrived at our present conception of valence. As long as the theory was in vogue, it was simply necessary to refer any given compound to some particular type. As soon as it was shown to which type a compound belonged, investigation ceased. The internal arrangement of the atoms was not inquired into. To conceive of the valence of atoms is to take a step beyond the theory of types, to find in the atoms themselves the reason for the types. Now that we have taken this step, it is unnecessary to retain the ideas of types at all. It has served its purpose and led to another idea, imperfect to be sure, but nevertheless more perfect than its predecessor. At present, it is not only necessary to show the resemblance between some molecule and a typical molecule, but, in every case, we have to determine which elements are in combination with each other. When, according to this latter principle, the constitution of a compound is determined, resemblances will show themselves between molecules belonging to the same type, but these resemblances will only be necessary consequences of the resemblances between the typical atoms of these molecules.

Residues.—By far the greater number of chemical compounds are more complicated than those with which we have thus far been dealing. Let us inquire into the cause of the complexity noticed in them.

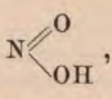
If we take any of the formulas above given, as, for instance, $H—Cl$, $H—O—H$,  NH_3, and  CH_4, and divide them at any part, we obtain two *residues* of equal valence. Thus, if we divide $H—Cl$, we obtain H and Cl, both univalent; if we divide $H—O—H$, we obtain H and OH, and these are both univalent, for, as can be readily seen, the group OH requires a univalent atom or group to saturate it; and this is what we understand by a univalent group. If we divide  NH_3, we obtain H and NH_2, or H_2 and NH; by the former division there are left two univalent, by the latter two bivalent factors. And so in the case of  $\mathrm{C}\begin{cases}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{cases}$; if we divide this formula, the following cases are possible: H and CH_3, H_2 and CH_2, H_3 and CH; leaving in the first case two univalent, in the second two bivalent, and in the third two trivalent, factors. This principle may be carried out further in connection with other and more complicated formulas, and thus are obtained the formulas of a great variety of these so-called residues; in most cases, however, the division made and the residues resulting may be compared to the simpler forms described. We speak of a water residue, OH, which, on account of the exceedingly important part it plays in the constitution of chemical compounds, has received a distinct name, *hydroxyl;* the ammonia residue, NH_2, is called *amide;* the residue NH is called *imide;* the methane residue, CH_3, is called *methyl;* the residue CH_2, *methylene*, etc. etc.

If we operate with the groups mentioned instead of with atoms alone, we shall find that we are able to build up a large number of formulas representing known compounds, as follows:—

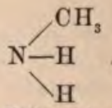
Similar to  $\mathrm{N}\begin{cases}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{cases}$, ammonia, we have:—


$\mathrm{N}\begin{cases}\mathrm{OH}\\ \mathrm{H}\\ \mathrm{H}\end{cases}$,

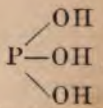
Hydroxylamine.


$\mathrm{N}\begin{cases}\mathrm{O}\\ \mathrm{OH}\end{cases}$,

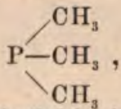
Nitrous acid.


$\mathrm{N}\begin{cases}\mathrm{CH_3}\\ \mathrm{H}\\ \mathrm{H}\end{cases}$,

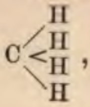
Methylamine.

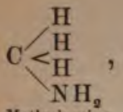

$\mathrm{P}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{cases}$,

Phosphorous acid.

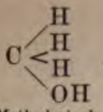

$\mathrm{P}\begin{cases}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{CH_3}\end{cases}$, etc.

Trimethylphosphine.

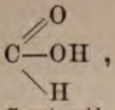
Similar to  $\mathrm{C}\begin{cases}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{cases}$, methane, we have:—



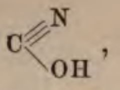
Methylamine.



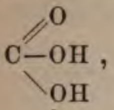
Methyl alcohol.



Formic acid.



Cyanic acid.



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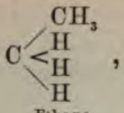
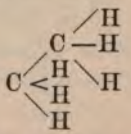
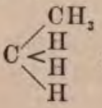
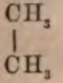


Ethane.

etc.

These residues are what were formerly known as radicles, though the term residue, as at present understood, is more comprehensive than the term radicle was. The conception of the residue is an exceedingly simple one, whereas there was considerable confusion in regard to the real meaning of the word radicle. It must be remembered that each of these residues has a constitution of its own, which becomes a part of the constitution of the compound into which it enters; but if we know the constitution of the compound from which the residue is derived, we also know the constitution of the residue. These residues are so well understood that, in writing graphic formulas, it is customary to indicate their presence by means of formulas which are not graphic. For instance, in the case of the compound ethane, above given, the complete graphic formula would be  ;

but, having once recognized the presence of the residue CH_3, we may write instead  ; or, even still simpler,  $\begin{matrix}CH_3\\|\\CH_3\end{matrix}$, for, as will be seen, the compound consists of a combination of two methyl groups, CH_3.

Chains.—A kind of combination which we have not yet considered consists in the union of two or more atoms of the same element, or of different elements, by a part of their affinities, thus forming *chains.* Examples of the first kind are met with particularly in the case of carbon. If two quadrivalent atoms of carbon unite in the simplest manner possible, we have a group, $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$, which must have six free affinities; if three such atoms unite, we have a group, $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$, which must have eight free affinities, etc.; and, as this chain combination may, as far as we know, be continued indefinitely, and the free affinities may be saturated by the greatest variety of atoms and residues, it is evident that the number of compounds, the possibility of whose existence is thus indicated, is unlimited.

We have examples of chains also among oxygen compounds, as we see in the following compounds:—

H—O—O—H, Cl—O—O—H, Cl—O—O—O—H,
Hydrogen peroxide. Chlorous acid. Chloric acid.

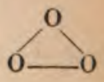
Cl—O—O—O—O—H, Br—O—O—O—H, etc.
Perchloric acid. Bromic acid.

The following are instances of chains formed by the union of atoms of different elements:—

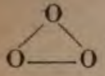
Cl—S—S—Cl, Cl—S—O—Cl, Cl—Se—O—Cl.
Sulphur chloride. Thionyl chloride Selenyl chloride.

H—O—S—O—O—H, H—O—O—S—O—O—H.
Sulphurous acid (?) Sulphuric acid.

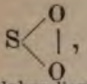
All the chains above given are of the variety known as *open chains.* Thus, in the compound Cl—O—O—O—H, the chain is —O—O—O—. At both its ends we have free affinities, capable of holding univalent atoms. If these two free affinities were to act upon each other, we might represent the resulting molecule thus .



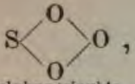
Here we have an example of a *closed chain.* If our conceptions in regard to the nature of ozone are correct, we have in it the above arrangement of atoms, viz.,



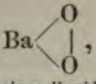
. Other examples of closed chains are seen in the formulas—



Sulphur dioxide.



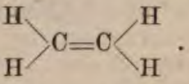
Sulphur trioxide.



Barium dioxide.

etc.

Double and Treble Union.—We have already seen that one atom may be combined with another by means of more than one affinity acting in each. In the compound $Ca=O$, for instance, two affinities of one atom are saturated by two affinities of another. This kind of union may occur in connection with atoms that have a higher valence than two. It is particularly met with in carbon compounds, as in C_2H_4, ethylene. In this compound, it is believed that the two carbon atoms are united by means of two affinities each, thus:

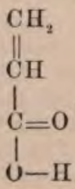


.

Further, in some compounds, a treble union is found between atoms of the same kind, as in acetylene, C_2H_2, in which it is believed that the carbon atoms are united by means of three affinities each, as follows:—

$$H—C\equiv C—H.$$

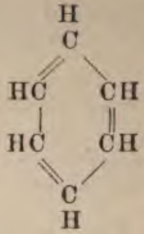
Lastly, in some compounds, it is believed that the carbon atoms are united partially by double and partially by single union, as, for instance, in



$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ C=O \\ | \\ O—H \end{array}$$

, which is the formula usually accepted for acrylic acid.

There are also a large number of compounds in which the carbon atoms are supposed to be united alternately by double and single union, and to form a closed chain, as in benzene:—



We have thus illustrated the manners in which atoms are believed to combine to form the various chemical compounds with which we have to deal. We are far from asserting that the formulas which we have given are in all cases satisfactorily proved. We entertain serious doubts in regard to many of them. Nevertheless, bearing in mind what is meant by the constitution of compounds, we believe that the formulas given represent, in the majority of cases, truths which are capable of proof. The proofs must, of course, in each case, remain relative, and cannot be absolute. We start with certain assumptions of atoms and the nature of atoms, and form a conception in regard to the constitution of the simplest compounds. Now, in so far as this conception is true, in just so far, in the majority of cases, we can prove the constitution of compounds. Just as soon as our ideas in regard to the constitution of hydrochloric acid change, our ideas of the constitution of all other compounds must also change. Whatever is true in our present conception of the constitution of hydrochloric acid, is also true in our conception of the constitution of other chemical compounds.

The proofs of the chemical constitution of compounds are of two kinds:—

1. Those which depend upon decomposing the compounds into simpler constituents, or the *analytical proofs*, and

2. Those which depend upon building the compounds up from simpler constituents, or the *synthetical proofs*.

In many cases we are able to obtain both of these proofs, and if then we reach the same results by both methods, these results are rendered doubly sure. In many cases, however, only one kind of proof can be given at present, but this may be so strong that the results are satisfactory. Where all proof is wanting, it is sometimes possible to propose a formula which very probably represents the constitution. Of this latter kind of formulas, viz., those which have not been proved, but may be shown to be extremely probable, we have a great many.

The methods of proof will be fully illustrated in the following section, in which we propose to consider the formulas of most of those chemical compounds which represent classes. The proofs for the formulas commonly accepted will be given in each case as fully as is compatible with a work of this nature. We do not necessarily undertake to give all the proofs, though we shall give enough to show clearly upon what foundations our constitutional formulas are based—enough to show that these formulas are entirely worthy of our careful study and our respect.

CLASSES OF COMPOUNDS.

Chemical compounds may be most conveniently classified according to their chemical properties. No system of classification which has been proposed, up to the present, can, in any sense, be called perfect, and yet the system now in most common use is convenient, and has a fair foundation in facts.

If we examine the compound which has the formula HCl, hydrochloric acid, and the compound which has the formula KOH, potassium hydroxide, we find that the two compounds differ very markedly from each other. The former has a taste which we call sour, the latter has the taste of lye, or an alkaline taste. The former will turn the color of many organic substances, while the latter will undo the work done by the former, restoring the original color. In whatever way we may consider these two compounds, we shall find that they have opposite or complementary properties. They are both chemically active substances, capable of producing marked changes in large numbers of other compounds. If they are brought together they neutralize each other, that is to say, they destroy each other's active properties and give rise to the formation of a new compound, differing entirely from the two which gave it birth. The two compounds, hydrochloric acid, HCl, and potassium hydroxide, KOH, are representatives of two great classes of compounds known as *acids* and *bases*. Many of the members of these two classes possess just as marked properties as do the two which have been mentioned, and for these the subdivision into acids and bases is rational and simple. But there are, further, some compounds which appear to possess the characteristics of both classes to a certain extent, and of neither class to any very great extent. For these compounds the system is not broad enough, though their number is not great. Probably, when the nature of the two classes of compounds is fully understood, no difficulty will be found in determining to which class any given compound belongs.

Acids.—The properties which characterize acids are the following:—

1. They have an acid or sour taste.
2. They change blue litmus red.
3. They act upon metals, hydrogen being evolved, and its place being taken by the metals, as, for instance:—

$$\underset{\text{Hydrochloric acid.}}{2(HCl)} + Zn = \underset{\text{Zinc chloride.}}{ZnCl_2} + 2H$$

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + Mn = \underset{\text{Manganese sulphate.}}{MnSO_4} + 2H$$

4. They act upon metallic hydroxides, forming neutral substances and water, as follows:—

$$\underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium chloride.}}{KCl} + H_2O$$

$$\underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Sodium hydroxide.}}{NaOH} = \underset{\text{Sodium nitrate.}}{NaNO_3} + H_2O$$

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Calcium oxide.}}{Ca(OH)_2} = \underset{\text{Calcium sulphate.}}{CaSO_4} + 2H_2O$$

Hydrogen Acids.—All acids contain hydrogen. They may consist of hydrogen and only one other element, or of hydrogen and a group of other elements of greater or less complexity. The constitution of those acids which consist of hydrogen and only one other element is, of course, very simple and readily understood. There are but few examples of this kind, some of which follow: Hydrochloric acid, HCl; hydrobromic acid, HBr; sulphydric acid, H_2S, etc. According to our conceptions of the nature of chemical constitution, compounds of the above formulas can only have one constitution.

It is a noticeable fact that acids of this first and simplest class never contain more than two atoms of hydrogen in the molecule; or, that no element with a higher valence than two forms these simple acids.

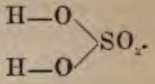
Hydroxyl Acids.—By far the greater number of acids belong to the second class mentioned. They consist of hydrogen and a group of greater or less complexity, as, for instance, $H(NO_3)$, nitric acid; $H(ClO_3)$, chloric acid; $H_2(SO_4)$, sulphuric acid, etc. In nearly all acids of this kind, oxygen is one of the constituents of the group with which the hydrogen is combined.

The hydrogen in these compounds is the changeable constituent. It is readily given up, and metals and groups are taken up in its place. The first question that would suggest itself, in considering the constitution of acids, would be this: In what manner is the hydrogen in them held in combination? It is believed that investigations thus far made, justify the answer that the hydrogen in these acids is almost always in combination with oxygen and, in a very few cases, with that element which is so similar to oxygen, viz., sulphur. The proofs for this statement cannot always be given. In the cases of many acids, there exist no independent proofs that in these the hydrogen is combined with oxygen. On the other hand, there are so many acids in which it can be satisfactorily shown that the hydrogen is in combination with oxygen that the above answer seems to be justified. We accordingly write the formulas of acids in such a way as to indicate the fact of union between oxygen and hydrogen thus:—

$(HO)NO_2$	$(HO)ClO_2$	$(HO)_2SO_2$
Nitric acid.	Chloric acid.	Sulphuric acid.

Or these same formulas may be made still more definite by writing them as follows:—

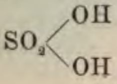
$H—O—NO_2$, $H—O—ClO_2$,



$$\begin{array}{l}H-O\diagdown\\ \qquad\quad SO_2.\\ H-O\diagup\end{array}$$

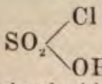
Proofs.—Under certain circumstances, an atom of oxygen and an atom of hydrogen may be removed from an acid containing oxygen, and one atom of chlorine then enters into the place occupied by the displaced atoms, and is held in combination. Now, the simplest conclusion we can draw is that the oxygen and hydrogen were present in the compound as a univalent group, viz., as (OH), or hydroxyl.

We have the following instances:—



$$SO_2\begin{array}{l}\diagup OH\\ \diagdown OH\end{array}$$

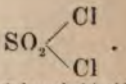
yields the compounds—



$$SO_2\begin{array}{l}\diagup Cl\\ \diagdown OH\end{array}$$

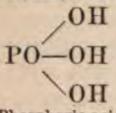
Sulphuryl oxichloride.

and



$$SO_2\begin{array}{l}\diagup Cl\\ \diagdown Cl\end{array}.$$

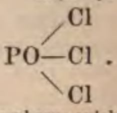
Sulphuryl chloride.



$$PO\begin{array}{l}\diagup OH\\ -OH\\ \diagdown OH\end{array}$$

Phosphoric acid.

yields



$$PO\begin{array}{l}\diagup Cl\\ -Cl\\ \diagdown Cl\end{array}.$$

Phosphorus oxichloride.

$C_2H_3O(OH)$	yields	$C_2H_3O—Cl$, etc.
Acetic acid.		Acetyl chloride.

Another reaction, which shows plainly that in these acids hydrogen is intimately associated with oxygen, is that by which the group NH_2 is introduced into them in the place of an atom of oxygen and an atom of hydrogen. The fact that the elements, oxygen and hydrogen, are displaced together indicates a connection between them in the compound.

We have the following instances:—

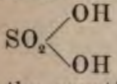
$C_2H_3O(OH)$ Acetic acid.	yields	$C_2H_3O(NH_2)$ Acetamide.
$C_7H_5O(OH)$ Benzoic acid.	yields	$C_7H_5O(NH_2)$. Benzamide.

These, with other general reactions, make up the proof of the statement above made, that, in most of those acids which contain oxygen, the characteristic hydrogen is in combination with oxygen in the form of hydroxyl (OH). In some few cases, as already mentioned, the oxygen is replaced by sulphur.

Further Experiments necessary in most Cases.—If we accept the presence of hydroxyl in oxygen acids, we are prepared to take another step. This hydroxyl may be in combination with only one element or with a group of elements. If it is in combination with only one element, the constitution of the resulting acid is easily understood. For instance, in the compound ClOH, hypochlorous acid, only one method of combination suggests itself, viz., Cl—O—H. There are very few examples of this kind.

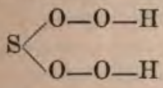
In those acids in which the hydroxyl is in combination with a group, the constitution is only then determined when, in addition to showing the presence of hydroxyl, the special constitution of the group itself is determined.

In sulphuric acid, for instance, after having determined the presence of two hydroxyl groups, we have the formula



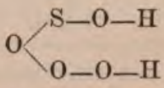
$$\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.$$

; but this formula only partially expresses the constitution of the acid. It remains to be shown in what manner the atoms are combined in the group SO_2, and also, with what atoms the hydroxyl groups are combined. Under the assumption that both sulphur and oxygen are bivalent elements, the constitution of sulphuric acid may be expressed by two different formulas, viz.:—



$$\mathrm{S}\left\langle\begin{matrix}\mathrm{O{-}O{-}H}\\ \mathrm{O{-}O{-}H}\end{matrix}\right.$$

and

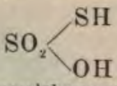


$$\mathrm{O}\left\langle\begin{matrix}\mathrm{S{-}O{-}H}\\ \mathrm{O{-}O{-}H}\end{matrix}\right. .$$

Special experiments must decide which of these formulas is the correct one.

Other Acids.—It has been mentioned that, in some acids, sulphur plays the part which oxygen plays in the hydroxyl-acids. In these we have the univalent group

(SH). The grounds for assuming the presence of this group in a compound are similar to those which lead to the assumption that the group (OH) is present. The two atoms S and H can both be removed from the compound and be replaced by one univalent atom, as chlorine; and, further, there is a general tendency for these two elements, sulphur and hydrogen, to leave the compound in company. Examples of acids of this kind are



$SO_2\left\langle\begin{matrix}SH\\OH\end{matrix}\right.$ and $CN(SH)$.

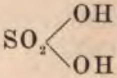
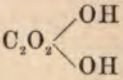
Hyposulphurous acid. Sulphocyanic acid.

Lastly, there is one acid which can be classified under none of the above heads. It contains hydrogen probably in combination with carbon, the latter being at the same time in combination with nitrogen. This is hydrocyanic acid, $H—C\equiv N$, in which the group CN acts like an element, making the compound analogous to hydrochloric acid, HCl.

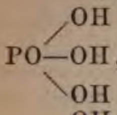
Subdivision of Acids.—It will be seen that different acids contain different numbers of hydroxyl-groups in their molecules. An acid which contains only one such group in its molecule has, of course, only one characteristic hydrogen atom. It is called a *monobasic* acid. An acid which contains two such groups in its molecule is a *bibasic* acid. We have, further, *tribasic*, *tetrabasic* acids, etc.

The same distinctions are possible among those acids which consist of hydrogen combined only with an element, and consequently do not contain hydroxyl; but as of these latter acids we have none which contain more than two atoms of hydrogen in the molecule, so we have among them only monobasic and bibasic acids.

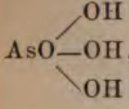
Examples:—

Monobasic acids.	Bibasic acids.
HCl, hydrochloric acid. $NO_2(OH)$, nitric acid. Cl(OH), hypochlorous acid.	 $SO_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$, sulphuric acid.
	 $C_2O_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$, oxalic acid.

Tribasic acids.



, phosphoric acid.



, arsenic acid.

Tetrabasic acids

$P_2O_3(OH)_4$, pyrophosphoric acid.

Bases.—Bases have properties which are the opposite of those possessed by acids. They all contain oxygen and hydrogen, and these elements are combined as hydroxyl, as may be shown in the same way that it was shown for acids. The most striking characteristic of bases is their power to act upon acids, forming neutral substances and water, as is seen in the following reactions:—

$$\underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{HNO_3} = \underset{\substack{\text{Potassium}\\\text{nitrate.}}}{KNO_3} + H_2O$$

$$\underset{\substack{\text{Calcium}\\\text{hydroxide.}}}{Ca(OH)_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4} + 2H_2O$$

Almost all bases consist of a metal combined with hydroxyl. Some few consist of a group of atoms combined with hydroxyl.

According to the valence of the metals with which the hydroxyl is combined, we have bases with one, two, three, etc., hydroxyl-groups in the molecule. Examples of these are the following:—

$K(OH)$, potassium hydroxide.
$Na(OH)$, sodium hydroxide.
$Ca(OH)_2$, calcium hydroxide.
$Ba(OH)_2$, barium hydroxide.
$Al(OH)_3$, aluminium hydroxide.
$Cr(OH)_3$, chromium hydroxide.
$Ti(OH)_4$, titanium hydroxide
$Zr(OH)_4$, zirconium hydroxide.

Differences between Acids and Bases.—The difference between acids and bases is dependent upon the nature of the elements or groups with which the hydroxyl is combined. The hydroxyl compounds of those elements which have a markedly metallic character are bases. The hydroxyl compounds of those elements which have a markedly non-metallic character are acids. If we consider the hydroxyl compounds of those elements which are neither markedly metallic nor non-metallic, we find that they sometimes act as acids and sometimes as bases. Thus the compound $SbO(OH)$, antimonyl hydroxide, is a weak base and a weak acid, exhibiting one property or the other according to the nature of the compound with which it is brought in contact.

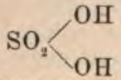
Complex Bases.—As above stated, there are a few bases which consist of hydroxyl combined with a group of atoms. Such, for instance, are

$BiO(OH)$	$UO(OH)$	$TiO(OH)_2$
Bismuthyl hydroxide.	Uranyl hydroxide.	Titanyl hydroxide.

In these compounds, as in the corresponding acids, the constitution of the group must be determined before we know the constitution of the compound. In the above cases, this determination is a simple matter. Bismuth conducts itself usually as a trivalent element; hence with the simplest kind of combination the group $—Bi=O$ will be univalent. Consequently the compound has the formula $O=Bi—O—H$.

Salts.—The neutral substances to which reference has been made as being formed by the action of acids upon bases are called salts. Salts may be considered either as acids in which the hydrogen has been replaced by a base residue, or as bases in which the hydrogen has been replaced by an acid residue. As the base residues are usually simpler than the acid residues, the former view is most commonly held, although the two views are, of course, identical.

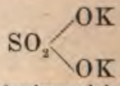
It is a simple matter to deduce the constitution of a salt from that of the acid and base or bases from which it is derived. Usually the hydrogen of the acid is replaced by one or more metals, the latter being held in combination by the same force or forces that held the former. Thus we have



$$SO_2\begin{cases} OH \\ OH \end{cases}$$

Sulphuric acid.

and



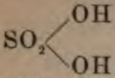
$$SO_2\begin{cases} OK \\ OK \end{cases}$$

Potassium sulphate.

$NO_2—OH$ and $NO_2—ONa$

Nitric acid. Sodium nitrate.

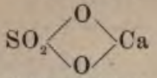
Or, a bivalent element may enter into an acid, in which case two hydrogen atoms will be replaced, thus:—



$$SO_2\begin{cases}OH\\OH\end{cases}$$

Sulphuric acid.

and

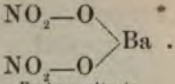


$$SO_2\begin{cases}O\\O\end{cases}Ca\ ;$$

Calcium sulphate.

$NO_2—OH$ and

Nitric acid.



$$\begin{matrix}NO_2—O\\NO_2—O\end{matrix}>Ba\ .$$

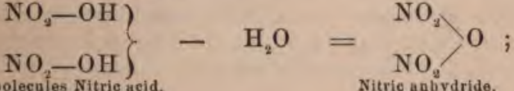
Barium nitrate.

Further complications are introduced when trivalent and quadrivalent elements enter into the composition of salts. From what has been said, however, the constitution of these salts will be readily understood.

Complex Salts.—Just as we have a few bases which consist of hydroxyl combined with groups of atoms, so we have salts which may be considered as derived from acids by the replacement of hydrogen by groups of atoms. Thus, a salt obtained from the acid $NO_2—OH$, and the base $UO—OH$, has the constitution expressed by the formula $NO_2—O—UO$. Here the hydrogen of the acid is replaced by the group UO, which is univalent.

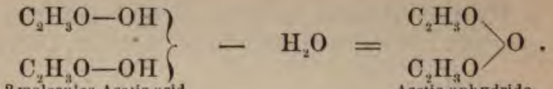
Anhydrides.—The constituents of water may be abstracted from many acids, and thus is formed a new class of compounds called anhydrides. The most striking characteristic of these compounds is their power to form acids with water, or to form salts by direct union with bases. The following are examples of anhydrides: Sulphuric anhydride, SO_3; nitric anhydride, N_2O_5; phosphoric anhydride, P_2O_5; acetic anhydride $(C_2H_3O)_2O$, etc.

When an anhydride is formed from a monobasic acid, two molecules must combine to furnish the hydrogen for the water. After the abstraction of the water, the two acid residues remain united, through the instrumentality of an atom of oxygen, thus:—



$$\left.\begin{matrix}NO_2—OH\\NO_2—OH\end{matrix}\right\}\ -\ H_2O\ =\ \begin{matrix}NO_2\\NO_2\end{matrix}>O\ ;$$

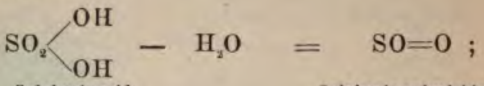
2 molecules Nitric acid. Nitric anhydride.



2 molecules Acetic acid.

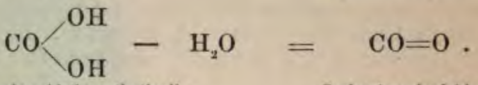
Acetic anhydride.

When an anhydride is formed from a bibasic acid, a molecule of water may be given off from a molecule of acid, thus:—



Sulphuric acid.

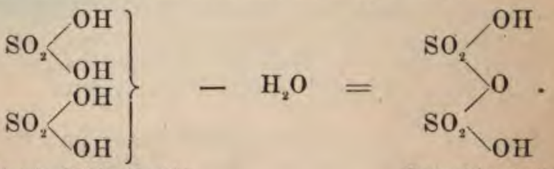
Sulphuric anhydride.



Carbonic acid (hypothetical).

Carbonic anhydride.

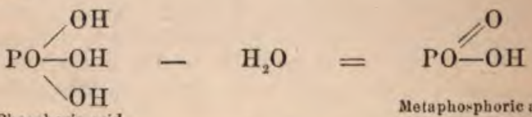
Or, two molecules of a bibasic acid may unite and give off one molecule of water, forming a compound which is, at the same time, an acid and an anhydride, thus:—



2 molecules Sulphuric acid

Pyrosulphuric acid.

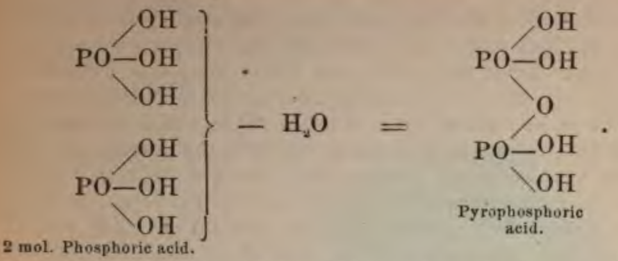
When an anhydride is formed from a tribasic acid, several possibilities may present themselves. 1. One molecule of the acid may lose one molecule of water, a compound being formed which is anhydride and acid, thus:—



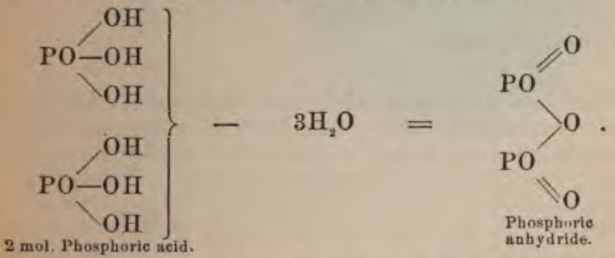
Phosphoric acid.

Metaphosphoric acid.

2. Two molecules of the acid may lose one molecule of water, a compound being formed which is a tetrabasic acid, and, at the same time, an anhydride:—



3. Two molecules of the acid may lose three molecules of water, a complete anhydride being formed:—

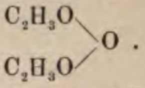


By combining a larger number of molecules of the acids and abstracting different numbers of molecules of water, a great variety of anhydrides might be produced, at least theoretically. Not many such complicated products are positively known, however.

From tetrabasic acids and acids with even higher basicity, corresponding anhydrides may be derived. With an increase in the basicity of the acids, the complexity of the resulting anhydride is, of course, increased.

Proofs of the Constitution of Anhydrides.—In regard to the correctness of the formulas given for these anhydrides, it can only be said that they are the simplest which we can conceive of. If we acknowledge that acetic anhydride, $(C_2H_3O)_2O$, consists of two acid-residues combined by an oxygen atom, then, by analogy, we must acknowledge that the other anhydrides, mentioned above, are constituted as represented by the formulas. But, can we assume any other formula for acetic anhydride? We know that the acid has the constitution $C_2H_3O(OH)$;

we know that the anhydride has the empirical formula, $C_4H_6O_3$, and that it is formed by the simple abstraction of water from the acid; we know that the hydroxyl group has the power to separate from the acid with comparative ease. What, then, is more natural than to assume that the water which is given off from the acid is formed from the hydroxyl groups, and that the groups C_2H_3O remain undecomposed? But this would give us, besides the water, two groups, C_2H_3O and an oxygen atom. These are all combined in one molecule, and, as we believe, in such a way that the oxygen atom exercises a linking power between the two groups or acid residues, giving the formula—

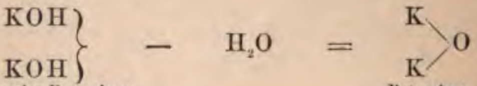


$$\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\!\!>O\ .$$

When an anhydride is formed by the abstraction of water from one molecule of an acid, the simplest conclusion we can draw is that an oxygen atom fills the place before occupied by two hydroxyl groups. We have no proof of this, to be sure, but it would be gratuitous to offer any other explanation of the formation of these anhydrides at present.

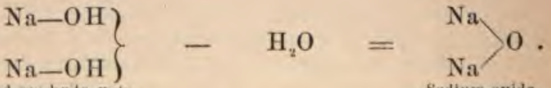
Oxides.—Just as anhydrides may be obtained from acids by the abstraction of water, so the oxides may be regarded as anhydrides of the bases. The consideration of the oxides is simpler than that of the anhydrides, because the bases themselves are generally simpler than the acids.

The simplest oxides are those obtained from the hydroxides of univalent elements, examples of which follow:—



$$\left.\begin{matrix}KOH\\KOH\end{matrix}\right\}\quad - \quad H_2O \quad = \quad \begin{matrix}K\\K\end{matrix}\!\!>O$$

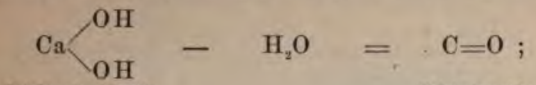
2 molecules Potassium hydroxide. Potassium oxide.



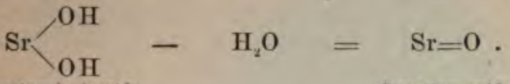
$$\left.\begin{matrix}Na{-}OH\\Na{-}OH\end{matrix}\right\}\quad - \quad H_2O \quad = \quad \begin{matrix}Na\\Na\end{matrix}\!\!>O\ .$$

Sodium hydroxide. Sodium oxide.

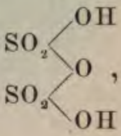
Of oxides obtained from the hydroxides of bivalent elements, we have, among others, the following:—

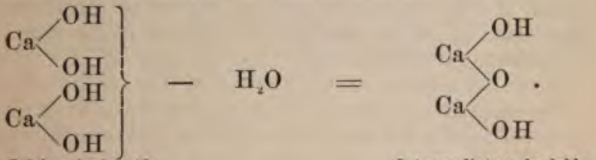


Calcium hydroxide. Calcium oxide.



Strontium hydroxide. Strontium oxide.

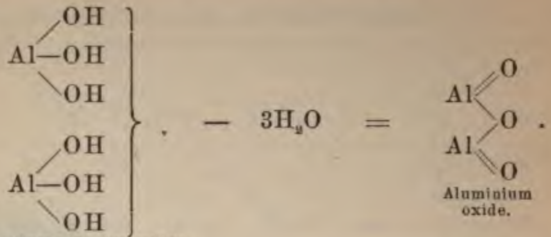
Theoretically, an intermediate anhydride may be derived, from either of the two preceeding oxides, analogous to the formation of pyrosulphuric acid, , from two molecules of sulphuric acid, thus:—



2 mol. Calcium hydroxide. Intermediate anhydride.

No such compounds have been obtained as yet. From the hydroxides of trivalent elements we may have more than one oxide formed. If one molecule of the hydroxide loses one molecule of water, a body is formed which is oxide and hydroxide at the same time. Reference has been made to these compounds (see *ante*, p. 118), under the head of bases. The compound AlO—OH may be regarded as derived from the hydroxide $Al(OH)_3$, by the loss of one molecule of water from one molecule of the hydroxide. It is both oxide and hydroxide.

The most common method of formation of oxides from hydroxides of trivalent elements consists in the union of two molecules of the hydroxide to lose three molecules of water, thus:—



2 mol. Aluminium hydroxide.

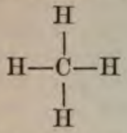
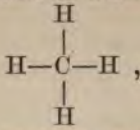
Aluminium oxide.

The principle of the formation of these oxides is thus seen to be the same as that of the formation of anhydrides. What was said in regard to the constitution of the latter holds good in regard to the constitution of the former. The view stated is the simplest which the facts permit.

Analogy between Salts and Anhydrides and Oxides.—As we saw above, a salt is either an acid in which the hydrogen is replaced by a base residue, or a base in which the hydrogen is replaced by an acid residue. In those salts which are derived from acids containing hydroxyl, we have a base residue and an acid residue united by means of oxygen. On the other hand, in many anhydrides, we have an acid residue and an acid residue united by means of oxygen, while in oxides, we have two base residues united by means of oxygen.

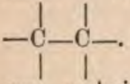
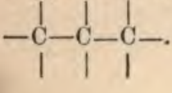
COMPOUNDS OF CARBON.

We have thus briefly considered the different classes of compounds, and have shown upon what foundations our ideas in regard to the general constitution of these classes of compounds rest. Among the compounds of carbon, we have many representatives of each of the classes above considered, and all that has been said holds good for these compounds; but owing to some peculiarities of carbon, which distinguish it from the other elements, certain things hold good for the carbon compounds in general, which do not hold good for the corresponding compounds of other elements. In the following paragraphs, therefore, the *general* formulas of the different classes of carbon compounds will be briefly treated.

Hydrocarbons.—Of the compounds of carbon those which it forms with hydrogen are, in general, the simplest, and, of the hydrocarbons, marsh-gas, or methane, CH_4, is the simplest one. With our present ideas in regard to constitution, there can be but one formula for this compound, viz.:  $\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & H \\ & & | & & \\ & & H & & \end{array}$, which represents merely that a quadrivalent atom of carbon is saturated by means of four hydrogen atoms. This is the most rational supposition which we can make with reference to this compound. The formula is certainly not proved, but it is exceedingly probable. As marsh-gas is a very important member of the group of carbon compounds, let us inquire more particularly concerning the grounds upon which the above formula is based. We first determine the empirical formula, CH_4, by means of analysis, and the determination of the specific gravity of the vapor of the compound. This formula is the expression of a fact and an hypothesis. The fact expressed is that methane contains 75 per cent. carbon and 25 per cent. hydrogen. The hypothesis is that the molecules of all chemical compounds, in the form of gas or vapor, have the same volume as a molecule of hydrogen. This hypothesis tells us the weights of the atoms contained in the molecule of methane and the weight of the molecule of methane, and hence, further, the number of atoms of carbon and hydrogen contained in the molecule. Knowing the above, it remains for us to determine in what manner these atoms are united, or, what is the same thing, to determine which atoms are in combination with each other. From our knowledge of hydrogen, we assume that it acts in this compound, as in all its other compounds, as a univalent element. But if it does act thus, then two hydrogen atoms cannot be united in the molecule CH_4, for, if they were, they could not remain a part of the molecule, as their affinities would be satisfied by their action upon each other. Consequently, the hydrogen atoms must all be in combination with the carbon atom. This result we express by the formula  $H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$, which is, further, in accordance with what we know concerning carbon, this element being in almost all cases quadrivalent.

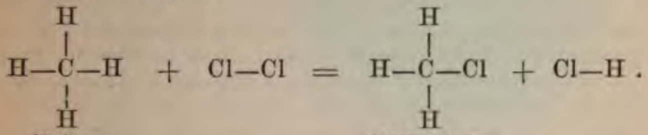
A question which would naturally suggest itself in connection with the compound CH_4 is this: Do all the hydrogen atoms play the same part in the molecule? In regard to this point, we can only say that, as far as investigations go, an affirmative answer to this question seems to be justified. If these hydrogen atoms were different, then, by replacing different ones by the same element or group, products should be obtained which are not identical. No such results have been reached, although the hydrogen atoms in methane have been replaced in a great variety of ways.

Homologous Series.—Starting with methane, we have a series of hydrocarbons of the general formula $C_n H_{2n+2}$. These resemble each other in many respects, and differ from each other in their formulas in a very simple way. The difference in the formulas of any two contiguous members of this series is CH_2. Such a series is called an *homologous series*. A number of similar series is known. In the methane series we have: Methane, CH_4; ethane, C_2H_6; propane, C_3H_8; butane, C_4H_{10}, etc.

The general principle according to which the members of this series are formed is found in the combination of the carbon atoms in open chains. Thus, as we have seen above, if two carbon atoms combine in the simplest manner possible, viz., by one of their affinities each, a chain is formed having six free affinities, as follows:  $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$. If three carbon atoms combine in the same way, a chain is formed having eight free affinities, thus:  $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$. In the same way, four carbon atoms combining would give a chain having ten free affinities, etc. etc. By saturating these free affinities by hydrogen, we would get compounds of the formulas C_2H_6, C_3H_8, C_4H_{10}, etc. etc., which are the formulas of the hydrocarbons above given.

Experimental Proofs.—Certain experiments have been performed which prove the correctness of the views in regard to the nature of the combination in the methane series of hydrocarbons.

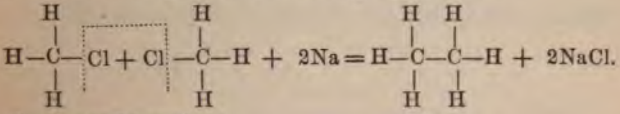
If methane is treated with chlorine, the following reaction takes place:—



$$H-C-H + Cl-Cl = H-C-Cl + Cl-H.$$

Methane. Chlormethane.

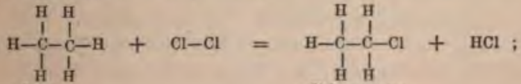
If the product is treated with sodium, the chlorine is extracted, and a compound of the formula C_2H_6 is obtained, according to the following equation:—



$$H-C-Cl + Cl-C-H + 2Na = H-C-C-H + 2NaCl.$$

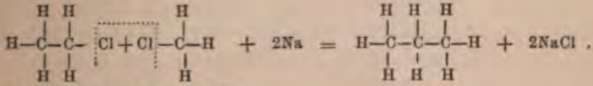
2 molecules Chlormethane. Ethane

With ethane similar reactions may be realized, and a product, C_3H_8, obtained, thus:—

1. 

$$H-C-C-H + Cl-Cl = H-C-C-Cl + HCl;$$

Ethane. Chlorethane.

2. 

$$H-C-C-Cl + Cl-C-H + 2Na = H-C-C-C-H + 2NaCl.$$

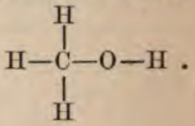
Chlorethane. Chlormethane. Propane.

It is perfectly plain that, by continuing these reactions with the new compounds obtained, we would have it in our power to build up a whole series of hydrocarbons corresponding to the series given above. If the combination always took place in the manner described, we should have simple chains, in which all the carbon atoms except those at the ends, would have two free affinities, while those at the ends would have three free affinities. The hydrocarbons themselves would be respectively:—

$$H_3C.CH_2.CH_2.CH_3;\ H_3C.CH_2.CH_2.CH_2.CH_3, \text{ etc. etc.}$$

These are called *normal hydrocarbons*, to distinguish them from others of the same general composition, but of different constitution, which will be treated of in a later paragraph.

Alcohols.—Running parallel to the series of hydrocarbons which we have just considered, is a series of compounds which may be looked upon as derived from the hydrocarbons by replacing a hydrogen atom in each by the univalent group OH, or hydroxyl. These compounds are to organic chemistry what the hydroxides of the metals are to inorganic chemistry. They are known as *alcohols*. The simplest of these is derived from methane and has the formula



$$\begin{array}{c} H \\ | \\ H—C—O—H \\ | \\ H \end{array} .$$

Proofs.—One of the hydrogen atoms of those alcohols which contain but one oxygen atom, differs from the others. It is easily replaceable by certain groups known as acid groups, which we shall consider hereafter. It is also replaceable by metals. In a compound of the formula CH_4O, we must assume that one hydrogen atom is in combination with the oxygen atom, while the other three are not, in order to account for its characteristic behavior. Again, if we treat the alcohol with HCl, the oxygen atom and the peculiar hydrogen atom are given off together, and their place is taken by a single atom of chlorine. This shows that the hydrogen and oxygen were present in the form of a univalent group, or as hydroxyl, which is the only form that satisfies these conditions.

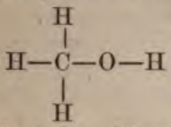
$$\underset{\text{Methyl alcohol.}}{H_3C—OH} + \underset{\text{Nitric acid.}}{H(NO_3)} = \underset{\text{Nitric ether.}}{H_3C—O(NO_2)} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Methyl alcohol.}}{H_3C\text{—}OH} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Chlormethane.}}{H_3C\text{—}Cl} + \underset{\text{Water.}}{H_2O}.$$

$$\underset{\text{Methyl alcohol.}}{H_3C\text{—}OH} + \underset{\text{Sodium.}}{Na} = \underset{\text{Sodium methylate.}}{H_3C\text{—}ONa} + \underset{\text{Hydrogen.}}{H}.$$

Further, the hydroxyl group can be introduced into the hydrocarbons and the alcohols thus obtained. In order to obtain the alcohol CH_4O, we start from chlormethane, CH_3Cl. If this is treated with the hydroxide of silver, the following reaction is realized:—

$$\underset{\text{Chlormethane.}}{CH_3Cl} + Ag(OH) = \underset{\text{Methyl alcohol.}}{CH_3.OH} + AgCl.$$

The above proofs suffice to show the correctness of the formula  $\begin{matrix} & & H & & & & \\ & & | & & & & \\ H & — & C & — & O & — & H \\ & & | & & & & \\ & & H & & & & \end{matrix}$ for the first member of the series of alcohols. Having once recognized the presence of hydroxyl in this alcohol, we would naturally expect to find it in the other alcohols. It is found in them all, and may be detected in the manner indicated in the case just considered.

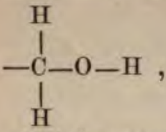
Classes of Alcohols.—It has been found that there are three distinct classes of alcohols, which have been called, respectively, *primary*, *secondary*, and *tertiary*. These differ from each other, in their properties, very markedly. This difference is particularly noticed when they are subjected to the influence of oxidizing agents, when they undergo change, as follows:—

Primary alcohols are converted first into aldehydes, and then into acids containing the same number of carbon atoms.

Secondary alcohols are converted into acetones, which, when further oxidized, yield acids with a smaller number of carbon atoms.

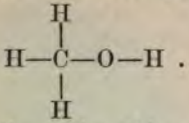
Tertiary alcohols are decomposed without previous formation of aldehydes or acetones, yielding acids with a smaller number of carbon atoms.

Primary Alcohols.—These differences in the properties are undoubtedly due to differences in constitution. In all primary alcohols we find that the group $CH_2.OH$, or



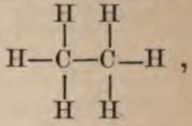
$$\begin{array}{cccccc} & H & & & & \\ & | & & & & \\ - & C & - & O & - & H \\ & | & & & & \\ & H & & & & \end{array}$$

, is present. This we saw in methyl alcohol, which is a compound of this group with hydrogen, thus:



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

. In ethyl alcohol, the next member of the series, this group is also present. This follows as soon as we acknowledge the presence of hydroxyl in the alcohols; for, in the compound



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

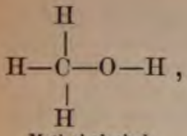
, it makes no difference which hydrogen atom is replaced by hydroxyl, the resulting compound will, in every case, have the same constitution and will necessarily contain the group $CH_2.OH$. In all alcohols which conduct themselves as primary, the presence of the group $CH_2.OH$ can be proved in a similar way. They are all derived from methyl alcohol by the replacement of a hydrogen atom with hydrocarbon residues of various composition and constitution.

By replacing a hydrogen atom with methyl, CH_3, ethyl alcohol, $CH_3.CH_2.OH$, is obtained.

By replacing a hydrogen atom with ethyl, C_2H_5, propyl alcohol, $C_2H_5.CH_2.OH$, is obtained.

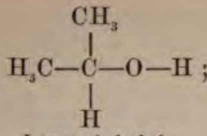
By replacing a hydrogen atom with propyl, C_3H_8, butyl alcohol, $C_3H_8.CH_2.OH$, is obtained, etc.

Secondary Alcohols.—If we replace two hydrogen atoms of methyl alcohol with hydrocarbon residues, alcohols are obtained which do not contain the group $CH_2.OH$, as is evident from the following examples:—



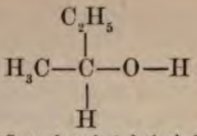
$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H$,

Methyl alcohol.



$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-O-H$;

Isopropyl alcohol.

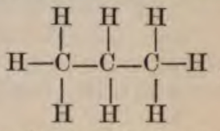


$H_3C-\overset{\displaystyle C_2H_5}{\underset{\displaystyle H}{C}}-O-H$.

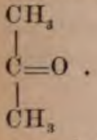
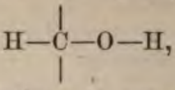
Secondary butyl alcohol.

These bodies contain the group CH.OH, and are representatives of secondary alcohols.

The simplest example of this class of bodies is isopropyl alcohol, the formula of which is given above.

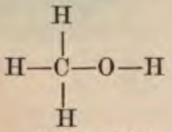
Proofs of the General Formula of Secondary Alcohols.—There are two alcohols of the formula, C_3H_8O. One of these conducts itself like the primary alcohols, and is hence supposed to contain the group CH_2.OH. An alcohol isomeric with the primary alcohol cannot contain the group CH_2.OH, but must contain the group CH.OH, as may be readily shown. Both of the alcohols are derived from the same hydrocarbon,  $H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$.

In this hydrocarbon there are only two kinds of hydrogen atoms, viz., those in combination with the central carbon atom, and those in combination with the terminal carbon atoms. If we replace any one of the latter by hydroxyl, we obtain primary propyl alcohol containing the group CH_2.OH. Whereas, if we replace one of the former hydrogen atoms by hydroxyl, we obtain secondary propyl alcohol containing the group CH.OH. Only these two cases are possible.

But, again, this secondary alcohol is prepared by allowing nascent hydrogen to act upon acetone. It will be shown that acetone can only have the constitution  $\begin{array}{l}CH_3\\ |\\ C=O\\ |\\ CH_3\end{array}$. Now, in being converted into secondary propyl alcohol, acetone takes up two atoms of hydrogen, and the only place where these hydrogen atoms can find entrance into the above molecule is at the central carbon atom. One of the bonds of union between the oxygen and carbon is loosened, and hydroxyl is formed; thus the carbon atom becomes possessed of a free affinity, which is at once saturated with hydrogen, and we have the group CH.OH or  $H-\overset{|}{\underset{|}{C}}-O-H$, which is bivalent.

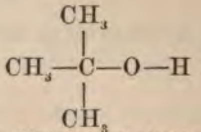
Similar considerations in connection with other secondary alcohols lead to similar results, and hence the conclusion is drawn that all secondary alcohols contain the group CH.OH.

Tertiary Alcohols.—If we replace three hydrogen atoms of methyl alcohol by hydrocarbon residues, alcohols are obtained which contain neither the group $CH_2.OH$, nor the group CH.OH, as may be seen in the following examples:—



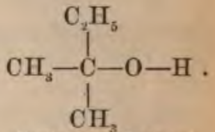
$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-H\ ,$$

Methyl alcohol.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-H\ ,$$

Tertiary butyl alcohol.



$$CH_3-\overset{\overset{C_2H_5}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-H\ .$$

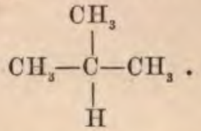
Tertiary amyl alcohol.

These bodies contain the group C.OH, and are representatives of tertiary alcohols.

The simplest example of this class of alcohols is tertiary butyl alcohol, $C_4H_{10}O$, the constitution of which is indicated by the formula given above.

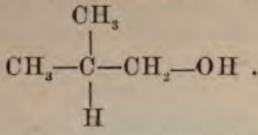
Proofs.—The proofs for the correctness of this formula are the following:—

There is a hydrocarbon, the formula of which can be shown to be



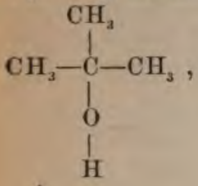
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_3\ .$$

From this, two alcohols are derived, one of which conducts itself as a primary alcohol, and the other of which does not. The former must have the formula



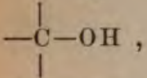
$$CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop H}{C}}-CH_2-OH\ .$$

The only alcohol derived from this hydrocarbon which is not a primary alcohol must have the formula



$$CH_3-\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle {| \atop O} \atop {| \atop H}}{C}}-CH_3\ ,$$

and hence contains the group



$$-\overset{|}{\underset{|}{C}}-OH\ ,$$

which is trivalent. Further, similar considerations of other tertiary alcohols indicate that in them also the group C.OH is contained; and consequently this is looked upon as the characteristic group of these bodies.

Determination of Alcohols.—With the knowledge thus gained with reference to alcohols in general, it is plain that we have it in our power to determine in any particular case, 1, whether the body we are dealing with is an alcohol; and, 2, whether it is a primary, secondary, or tertiary alcohol. The first thing to be done is to determine whether the body contains hydroxyl or not. Treatment with the chlorides of phosphorus, either the terchloride or pentachloride, is one of the best means of making this determination. If by treatment with the chloride a product is obtained containing one atom of chlorine in the molecule in the place of an oxygen atom and a hydrogen atom, we can assume that hydroxyl was present. If this hydroxyl is the alcoholic hydroxyl, then its hydrogen must be capable of replacement by the so-called acid groups. To determine this, acetyl chloride, $C_2H_3O.Cl$, is very frequently employed. If this body is allowed to act upon a substance containing an alcoholic hydroxyl group, the chlorine of the chloride combines with the hydrogen of the hydroxyl, forming hydrochloric acid, and the acid group C_2H_3O takes the place of the hydrogen, thus:—

$$\underset{\text{Alcohol.}}{R{-}OH} + \underset{\text{Acetyl chloride.}}{C_2H_3O.Cl} = \underset{\text{New product.}}{R{-}O{-}C_2H_3O} + HCl.$$

If the reaction takes place in this manner, we are justified in concluding that the hydroxyl group is alcoholic, or that the body under examination is an alcohol.

It remains still to determine whether the alcohol is primary, secondary, or tertiary. This can be accomplished by subjecting it to the influence of oxidizing agents.

If it yields an aldehyde, and then an acid containing the same number of carbon atoms, it is a primary alcohol.

If it yields first an acetone, and then by further oxidation breaks up, yielding an acid or acids containing a smaller number of carbon atoms, it is a secondary alcohol.

If, without first yielding an aldehyde or an acetone, it breaks up directly with the formation of an acid containing a smaller number of carbon atoms, it is a tertiary alcohol.

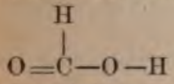
The above tests then enable us to determine a part of the constitutional formulas of many compounds. If we have by means of these tests determined that a compound is a primary alcohol, we assume that it contains the group $CH_2.OH$. If it is a secondary alcohol, it contains the group $CH.OH$. And, if it is a tertiary alcohol, it contains the group $C.OH$. But these groups may enter into a great variety of compounds; and frequently, after we have determined the presence of one or the other of these groups, it would still be necessary to determine the constitution of the group with which it is combined. These special determinations will be considered later.

Mercaptans.—If in place of hydroxyl, in the alcohols we have considered, we introduce the group HS, bodies are obtained which have been called mercaptans. These are in many respects analogous to alcohols, though in their reactions they differ from them somewhat. Their constitution is the same as that of the alcohols. The principal method for their formation consists in the action of potassium sulphydrate, KSH, on the chlorides of alcohol residues. These latter are obtained by replacing the hydroxyl of alcohols by chlorine, and the reaction for the formation of the mercaptans takes place as follows:—

$$\underset{\text{Alcoholic chloride.}}{RCl} + K{-}SH = \underset{\text{Mercaptan.}}{R{-}SH} + KCl.$$

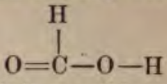
It will thus be seen that the group SH occupies the place which was occupied by the group OH in the original alcohol. Theoretically, a mercaptan may be prepared corresponding to every alcohol. Thus we might have primary, secondary, and tertiary mercaptans, corresponding to all the known primary, secondary, and tertiary alcohols. Only such mercaptans have been prepared up to the present as correspond to the primary alcohols.

Acids.—What has been said above concerning acids in general is true of the acids of carbon. They contain hydroxyl, and possess the properties which we have recognized as belonging to acids. In general, they are weaker than other acids, though they differ among each other in strength between comparatively wide limits. We have several series of acids of carbon, corresponding to the series of hydrocarbons and alcohols. The simplest carbon acid is derived from methane, and has the formula



$$O{=}\overset{\overset{\displaystyle H}{|}}{C}{-}O{-}H$$

. It differs from the simplest alcohol in containing an atom of oxygen in the place of two atoms of hydrogen. Just as this alcohol consists of hydrogen combined with the group $CH_2.OH$, so the acid consists of hydrogen combined with the group $CO.OH$. This is the characteristic group of the acids of carbon.

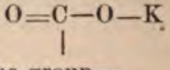
Proofs.—In the first place, the presence of hydroxyl is proved the same as in the case of ordinary acids. In the acid H_2CO_2, if we assume the presence of hydroxyl, we have the formula $HCO{-}OH$. Further, the other hydrogen atom contained in the acid does not conduct itself as if it were in combination with oxygen, but the same as hydrogen atoms which are in combination with carbon directly. No changes which the acid undergoes indicate any connection between this hydrogen atom and oxygen atom, so we may conclude that they are not present as hydroxyl. But, if they are not present as hydroxyl, they must be united directly with the carbon atom, and the formula is  $H{-}C(=O){-}O{-}H$ . . . Now by certain appropriate reactions, it is possible to replace that hydrogen atom in this acid which is in direct combination with the carbon by groups such as CH_3, C_2H_5, etc. The compounds thus obtained must contain the group $CO.OH$. They possess all the properties of acids.

Methods for the Formation of the Acids of Carbon.—The methods of preparation of the acids of carbon enable us also to judge of their constitution. Some of these methods may be briefly described.

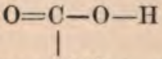
1. The simplest acid, above referred to, viz., H_2CO_2, is obtained by bringing carbon monoxide, CO, together with potassium hydroxide, KOH. The two substances combine directly, yielding the potassium salt of the above acid, thus:—

$$CO + KOH = HCO_2K.$$

From this experiment we conclude that, in the salt, one of the oxygen atoms is in direct combination with carbon, as it was in carbon monoxide, while the other oxygen atom serves the purpose of linking the carbon atom to the potassium. Hence the group—

$COOK$ or  $O{=}\overset{}{\underset{|}{C}}{-}O{-}K$

is present in the salt, and the group—

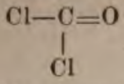
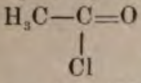
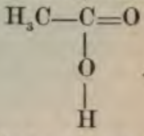
 $O{=}\underset{|}{C}{-}O{-}H$ in the acid.

2. When methane, CH_4, is allowed to act upon carbonyl chloride, $COCl_2$, one of the chlorine atoms is replaced by the residue CH_3, thus:—

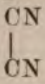
$$\text{(I.)}\quad CH_4 + COCl_2 = CH_3.COCl + HCl.$$

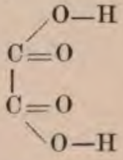
When the product is treated with water, the second chlorine atom is replaced by OH, as follows:—

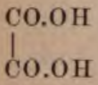
$$\text{(II.)}\quad CH_3.COCl + HHO = CH_3.CO.OH + HCl.$$

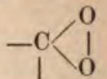
Now carbonyl chloride is obtained by the direct addition of Cl_2 to carbon monoxide, CO; and hence must have the constitution  $\begin{array}{l}\mathrm{Cl{-}C{=}O}\\ \quad\;|\\ \quad\mathrm{Cl}\end{array}$. The simplest interpretation of reaction (I.) above is that the residue CH_3 takes the place occupied by one of the chlorine atoms, which would give  $\begin{array}{l}\mathrm{H_3C{-}C{=}O}\\ \qquad\;\;|\\ \qquad\;\mathrm{Cl}\end{array}$. Lastly, the simplest interpretation of reaction (II.) is that the hydroxyl group enters into the place of the second chlorine atom, which gives as the constitution of the product  $\begin{array}{l}\mathrm{H_3C{-}C{=}O}\\ \qquad\;\;|\\ \qquad\;\mathrm{O}\\ \qquad\;\;|\\ \qquad\;\mathrm{H}\end{array}$.

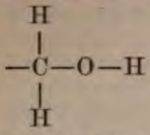
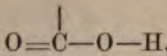
This product is acetic acid, a homologue of the simplest acid of carbon. It contains the group CO.OH.

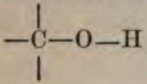
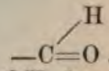
3. The compound cyanogen,  $\begin{array}{l}\mathrm{CN}\\ |\\ \mathrm{CN}\end{array}$, is converted into an acid by the action of water. This acid has the formula $C_2H_2O_4$. It is a bibasic acid, and hence contains two hydroxyl groups, which would lead to the formula $C_2O_2(OH)_2$. As both the hydroxyl groups conduct themselves in exactly the same way, it is concluded that they are combined in exactly the same way. The only formula that satisfies these conditions is



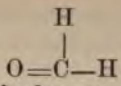
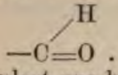
, or  $\begin{array}{l}\mathrm{CO.OH}\\ |\\ \mathrm{CO.OH}\end{array}$. In this compound we have two groups CO.OH, and, as we have seen, it is a bibasic acid. There are a great many compounds containing the group CN acting as a univalent group. By treating these with solutions of metallic hydroxides, the nitrogen is given off in the form of ammonia, NH_3, and in its place are taken up two atoms of oxygen and an atom of a univalent element. The group with which the CN is in combination remains unchanged. Hence, in accordance with the above experiment, it is believed that this reaction consists in a conversion of the group CN into COOH or COOM, in which M represents one atom of a univalent metal. The constitution of this group is, of course, expressed as above by the formula $O{=}\underset{|}{C}{-}O{-}M$. All the substances thus prepared and containing this group are derivatives of the acids; they are salts.

4. The acids are derived from primary alcohols by simple oxidation. When an acid is obtained from either a secondary or a tertiary alcohol, a complex oxidation takes place; the molecule must be broken up and rearranged. We have seen that the difference between the three classes of alcohols is due to the difference in the characteristic groups of each class; these being CH_2OH, CHOH, and $\dot{C}OH$. The oxidation consists in the abstraction of hydrogen and addition of oxygen. If hydrogen is abstracted from and oxygen added to the group CH_2OH, we obtain $\dot{C}OOH$ or $O{=}\overset{|}{C}{-}O{-}H$. If we abstract hydrogen from and add oxygen to the group CHOH, which is bivalent, we could not obtain another bivalent group, unless it be one with an exceedingly improbable formula as, for instance,  , and this would contain no hydrogen, so that it could not be considered as characteristic of acids. Lastly, the group COH cannot lose hydrogen and gain oxygen and still remain trivalent. As then the only alcohols which can yield the group COOH by the oxidation of their own characteristic group are the primary alcohols, and as those alcohols which cannot yield this group by such oxidation do not yield corresponding acids, the con-

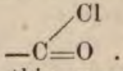
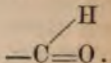
clusion is drawn that the change which takes place when primary alcohols are oxidized consists in the conversion of the group  $-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-H$ into  $O=\overset{|}{C}-O-H$, which is a necessary constituent of carbon acids.

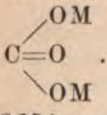
Aldehydes.—Aldehydes are products derived from the partial oxidation of primary alcohols, the group CH_2OH being converted into COH. This group is not identical with the group  $-\overset{|}{\underset{|}{C}}-O-H$ of tertiary alcohols, but has the constitution expressed by the formula  $-\overset{\diagup H}{C}{=}O$. It is a univalent group, just as the group CH_2OH, from which it is derived, is univalent; whereas, the tertiary alcohol group, COH, is trivalent. The aldehydes are intermediate products between primary alcohols and the acids which these yield. It was shown that the acids are formed from these alcohols by the extraction of hydrogen and addition of oxygen. If hydrogen is only abstracted and no oxygen added, the product is an aldehyde, thus:—

$R-CH_2OH$,	$R-COH$,	$R-COOH$.
Primary alcohol.	Aldehyde.	Acid.

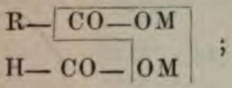
Proofs.—The proofs of the general constitution of aldehydes are similar to those given for the acids. Take, for instance, the simplest aldehyde. This has the formula H_2CO. The tests for the presence of hydroxyl, above considered, if applied to aldehydes, show that the group is not present. On the contrary, if the aldehydes be treated with the chloride of phosphorus, the oxygen atom is extracted and its place is taken by *two* chlorine atoms. This shows that the oxygen was held in combination by two affinities of the carbon atom, and, consequently, it could not have been present in combination with hydrogen, forming hydroxyl. We are thus led to the formula  $O{=}\overset{\overset{H}{|}}{C}{-}H$ for the above compound. It consists of a hydrogen atom combined with the group  $-\overset{\diagup H}{C}{=}O$. Other aldehydes are derived from this simplest one by replacing one of the hydrogen atoms with a residue of greater or less complexity. Thus, we may introduce the group CH_3 or C_2H_5, and we would obtain the compounds $CH_3{-}COH$ and $C_2H_5{-}COH$ respectively, both of which are aldehydes.

The methods for the preparation of aldehydes also furnish proof of the constitution above ascribed to them. Some of these are the following:—

1. We have already seen, that, when acids are treated with the chlorides of phosphorus, their hydroxyl is replaced by an atom of chlorine, yielding chlorides of acid residues. Each such chloride, as was shown, contains the group  $-\overset{\diagup Cl}{C}{=}O$. If we could replace the chlorine atom in this group by hydrogen, we would plainly have the characteristic aldehyde group  $-\overset{\diagup H}{C}{=}O$. Such a replacement has been effected in the cases of some of the chlorides, and the resulting bodies were found to be the expected aldehydes.

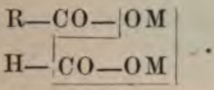
2. When a salt of any acid of carbon is mixed with a salt of the simplest acid of carbon (formic acid), of the formula H.CO.OH, and the mixture distilled, an aldehyde is obtained together with a carbonate. The carbonates are derived from a bibasic acid, and have the formula  $\overset{\diagup OM}{\underset{\diagdown OM}{C}}{=}O$. It seems rational to suppose that the groups OM have passed directly from the compounds in which they were originally contained to the carbonate, and that the group CO also has been derived directly from one of the original acids. If these suppositions are correct,

then we are led to the conclusion that the aldehyde resulting from the described reaction contains the group $-\overset{H}{\overset{/}{C}}=O$. For, let R—CO.OM represent the formula of any salt of a carbon acid, and H.CO.OM a salt of formic acid. On bringing these two compounds together and heating them, either one of two things can take place if the above suppositions are correct. The groups forming the carbonate may be split off thus:—



$$\begin{array}{l} R—\boxed{CO—OM} \\ H—CO—\boxed{OM} \end{array} ;$$

or, thus:—

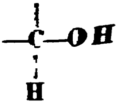
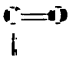
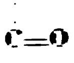
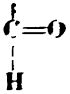
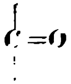
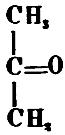


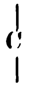
$$\begin{array}{l} R—CO—\boxed{OM} \\ H—\boxed{CO—OM} \end{array} .$$

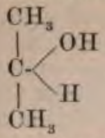
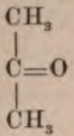
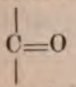
The remaining groups, uniting in the simplest way, will give us, in the first place, a compound, $R-\overset{H}{\overset{/}{C}}=O$, and, in the second place, a compound of exactly the same constitution.

3. Aldehydes are formed only from primary alcohols, not from secondary or tertiary alcohols. If we examine the group characteristic of the alcohols, we shall find that the only one of them which is capable of transformation into the group $-\overset{H}{\overset{/}{C}}=O$ is that of primary alcohols, $-CH_2OH$; and, further, the group $-\overset{H}{\overset{/}{C}}=O$ is the only one containing carbon, hydrogen, and oxygen in the same proportions which can be derived from the group of primary alcohols, and not from those of secondary and tertiary alcohols.

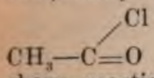
These considerations make it exceedingly probable that all aldehydes contain the group $-\overset{H}{\overset{/}{C}}=O$, as above stated.

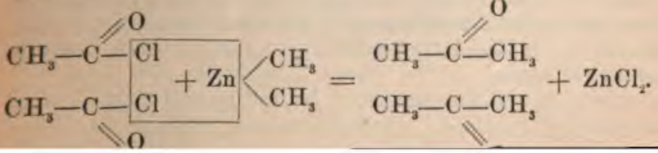
Acetones. — Acetones are products of the partial oxidation of secondary alcohols, the group  $-\overset{|}{\underset{|\atop H}{C}}-OH$ being converted into the group  $\underset{|}{C}=O$. The aldehydes, too, contain the group  $\overset{|}{\underset{|}{C}}=O$: but it is further characteristic of aldehydes that one of the affinities of this group is saturated with hydrogen, giving the complete group  $\overset{|}{\underset{|\atop H}{C}}=O$. On the other hand, it is characteristic of acetones that both of the affinities of the group  $\overset{|}{\underset{|}{C}}=O$ are saturated with hydrocarbon residues. Thus the simplest acetone known has the formula  $\overset{CH_3\atop |}{\underset{|\atop CH_3}{C}}=O$, both the affinities of the characteristic group being saturated with residues of the hydrocarbon methane, CH_4.

Proofs.—As just stated, the simplest acetone has the formula C_3H_6O. If a chloride of phosphorus be allowed to act upon this compound, the result is similar to that obtained in the same experiment with aldehydes, viz., the atom of oxygen is abstracted, and two chlorine atoms take its place. This shows that the oxygen was not present as hydroxyl, but was combined with the carbon atom by means of two affinities, forming the group  $\overset{|}{\underset{|}{C}}=O$.

Again, if nascent hydrogen is allowed to act upon this acetone, secondary propyl alcohol is the product, and the alcohol has the formula . From this we conclude that in acetone, as well as in secondary propyl alcohol, the two groups CH$_3$ are present; and we are thus led to the formula  $\begin{array}{c} CH_3 \\ | \\ C=O \\ | \\ CH_3 \end{array}$ for the simplest acetone. We recognize in this formula what we have stated to be the characteristic of all acetones, viz., it consists of two hydrocarbon residues combined by means of the bivalent group  $\begin{array}{c} | \\ C=O \\ | \end{array}$.

The following methods of preparation serve as proofs of the accepted constitution of acetones:—

1. Just as aldehydes are obtained from acid chlorides by replacing the chlorine with hydrogen, so acetones are obtained from the same chlorides by replacing the chlorine with hydrocarbon residues. By treating acetyl chloride, $C_2H_3O.Cl$, with zinc methyl, $Zn(CH_3)_2$, ordinary acetone, $CO(CH_3)_2$, is produced, together with zinc chloride, $ZnCl_2$. The formula of acetyl chloride is known to be . Hence the simplest interpretation of the above reaction is that a methyl group of zinc methyl takes the place of a chlorine atom in acetyl chloride, thus:—



And this leads us clearly to the formula above assumed as representing the constitution of acetone.

2. When the salts of many acids of carbon are subjected to dry distillation, acetones are formed, together with a carbonate or carbonates. This reaction is analogous to the reaction for the preparation of aldehydes, by the distillation of a mixture of the salt of some carbon acid and a salt of formic acid. What was said in regard to the latter reaction, showing that the group $\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{=O}$ must be present in aldehydes, holds good in regard to the reaction under consideration, and shows just as conclusively that the group $\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{=O}$ must be present in acetones. Let R.CO.OM represent a salt of an acid of carbon. Its decomposition by heat may be represented as follows:—

$$\begin{array}{l}\mathrm{R.}\boxed{\mathrm{CO.OM}}\\ \mathrm{R.CO.}\boxed{\mathrm{OM}}\end{array}.$$

The residues uniting, we have a compound, R—CO—R, which has the general formula of an acetone, as above assumed. Or let R.COOM represent the salt of one carbon acid and R′.COOM the salt of another carbon acid, in which R and R′ are both hydrocarbon residues. The decomposition, which takes place when a mixture of these two salts is heated, is represented as follows:—

$$\begin{array}{l}\mathrm{R.}\boxed{\mathrm{COOM}}\\ \mathrm{R'.CO}\boxed{\mathrm{OM}}\end{array}.$$

This gives a compound of the formula R—CO—R′.

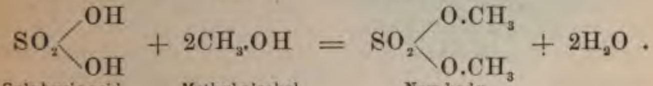
It will be seen that one of the first conditions for the production of an acetone by means of this reaction is that neither of the salts employed be a formate, H.COOM, as the use of the latter would give rise to the formation of an aldehyde.

3. Acetones are produced by the partial oxidation of secondary alcohols. Considerations, similar to those

employed in the cases of acids and aldehydes, show that the supposition, that the group $\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{O}$ is present in acetones, is most in harmony with the fact of the ready transformation of secondary alcohols into acetones.

Ethers.—When acids and bases, in general terms, act upon each other, salts are formed, water being eliminated. Just so when alcohols and carbon acids act upon each other, bodies, similar to salts, are formed, water being eliminated:—

$$\underset{\text{Formic acid.}}{\mathrm{H.COOH}} + \underset{\text{Alcohol.}}{\mathrm{C_2H_5.OH}} = \underset{\text{New body.}}{\mathrm{H.CO.OC_2H_5}} + \mathrm{H_2O};$$



$$\underset{\text{Sulphuric acid.}}{\mathrm{SO_2}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\end{cases}} + \underset{\text{Methyl alcohol.}}{\mathrm{2CH_3.OH}} = \underset{\text{New body.}}{\mathrm{SO_2}\begin{cases}\mathrm{O.CH_3}\\ \mathrm{O.CH_3}\end{cases}} + \mathrm{2H_2O}.$$

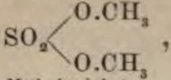
$$\underset{\text{Nitric acid.}}{\mathrm{NO_2{-}OH}} + \underset{\text{Alcohol.}}{\mathrm{C_2H_5{-}OH}} = \underset{\text{New body.}}{\mathrm{NO_2{-}OC_2H_5}} + \mathrm{H_2O}.$$

It will be seen that these bodies differ from salts in that they contain hydrocarbon residues in the place of metals. Salts were defined as acids in which the hydrogen of the hydroxyl group is replaced by a base residue. These bodies are acids in which the hydrogen of the hydroxyl group is replaced by a hydrocarbon residue. All bodies of this kind are called ethers, and to distinguish them from another class of bodies known as *simple ethers*, and which will be considered below, they are usually known as *compound ethers.* The analogy between compound ethers and salts is very close, and hence, if the nature of salts is understood, the nature of these ethers will also be readily understood. We may have compound ethers derived from monobasic, bibasic, tribasic, etc. acids, and we may have compound ethers containing univalent, bivalent, trivalent, etc. hydrocarbon residues; as, for instance,

Ethers from monobasic acids:—

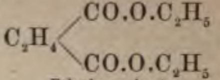
$$\underset{\text{Ethyl nitrate.}}{\mathrm{NO_2.O.C_2H_5}}, \qquad \underset{\text{Methyl acetate.}}{\mathrm{CH_3.CO.O.CH_3}}, \qquad \text{etc.}$$

Ethers from bibasic acids:—



$$SO_2\begin{matrix}\diagup O.CH_3\\ \diagdown O.CH_3\end{matrix},$$

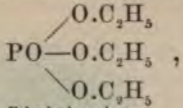
Methyl sulphate.



$$C_2H_4\begin{matrix}\diagup CO.O.C_2H_5\\ \diagdown CO.O.C_2H_5\end{matrix},\quad \text{etc.}$$

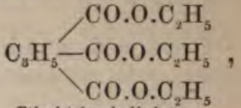
Ethyl succinate.

Ethers from tribasic acids—



$$PO\begin{matrix}\diagup O.C_2H_5\\ —O.C_2H_5\\ \diagdown O.C_2H_5\end{matrix},$$

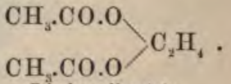
Ethyl phosphate.



$$C_3H_5\begin{matrix}\diagup CO.O.C_2H_5\\ —CO.O.C_2H_5\\ \diagdown CO.O.C_2H_5\end{matrix},\quad \text{etc.}$$

Ethyl tricarballylate.

The above ethers all contain univalent hydrocarbon residues. Among those containing bivalent residues may be mentioned—



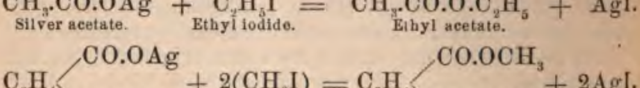
$$\begin{matrix}CH_3.CO.O\diagdown\\ CH_3.CO.O\diagup\end{matrix}C_2H_4\ .$$

Ethylene diacetate.

Proofs.—The fact that compound ethers are, in many cases, formed by the direct action of acids upon alcohols, and that water is formed at the same time, taken together with our knowledge concerning the constitution of acids and alcohols, points clearly to the constitution for these ethers which has been above assumed. But another method of formation is just as decisive in its testimony.

If the silver salts of acids are treated with the chlorides, bromides, or iodides of hydrocarbon residues, compound ethers are formed in which the hydrocarbon residues are found in the place of the silver which was in the salts, and the silver itself is found in combination with the chlorine, bromine, or iodine which was in combination with the hydrocarbon residues. This is seen in the following typical reactions:—

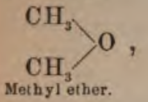
$$\underset{\text{Silver acetate.}}{CH_3.CO.OAg} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl acetate.}}{CH_3.CO.O.C_2H_5} + AgI.$$

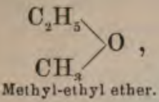


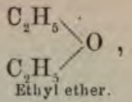
$$C_2H_4\begin{matrix}\diagup CO.OAg\\ \diagdown CO.OAg\end{matrix} + 2(CH_3I) = C_2H_4\begin{matrix}\diagup CO.OCH_3\\ \diagdown CO.OCH_3\end{matrix} + 2AgI.$$

Silver succinate. Methyl iodide. Methyl succinate.

Simple Ethers.—Simple ethers correspond to the metallic oxides. They consist of two hydrocarbon residues united by means of an oxygen atom, just as the metallic oxides consist of two base residues united by means of an oxygen atom. Examples of these are the following:—


Methyl ether.


Methyl-ethyl ether.


Ethyl ether.

etc.

Proofs.—The constitution of these compounds is rendered clear by a consideration of one of the principal methods of their formation.

When an alcohol is treated with sodium or potassium, as we have seen, the hydrogen of the hydroxyl is replaced by the metal employed. We thus obtain compounds such as sodium ethylate $C_2H_5.ONa$, sodium methylate $CH_3.ONa$, etc. If these compounds are further treated with the iodides of hydrocarbon residues, the iodine combines with the metal and the residues unite. Thus we have the following reactions:—

$$\underset{\text{Sodium ethylate.}}{C_2H_5.ONa} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl ether.}}{C_2H_5—O—C_2H_5} + NaI,$$

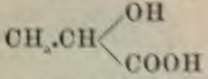
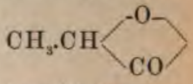
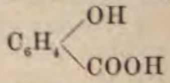
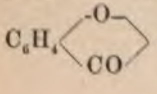
$$\underset{\text{Sodium methylate.}}{CH_3.ONa} + \underset{\text{Methyl iodide.}}{CH_3I} = \underset{\text{Methyl ether.}}{CH_3—O—CH_3} + NaI,$$

$$\underset{\text{Sodium methylate.}}{CH_3.ONa} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Methyl-ethyl ether.}}{CH_3—O—C_2H_5} + NaI,$$

$$\underset{\text{Sodium ethylate.}}{C_2H_5.ONa} + \underset{\text{Methyl iodide.}}{CH_3I} = \underset{\text{Methyl-ethyl ether.}}{C_2H_5—O—CH_3} + NaI.$$

From these reactions we see what the constitution of the ethers formed must be. We are in each case justified in assuming that the hydrocarbon residue enters into the new compound in the place occupied by the metal, and, according to our conceptions concerning alcohols, this metal is united to the rest of the molecule in which it is contained by means of an oxygen atom.

Anhydrides.—The anhydrides of carbon compounds are derived from carbon acids in the same way that anhydrides in general are derived from acids; and all the possibilities which we considered above hold good for these anhydrides. There are anhydrides derived from monobasic, bibasic, tribasic acids, etc. There are partial and complete anhydrides: but, further, there are anhydrides derived from compounds which partake of the double character of alcohol and acid. In these compounds the hydroxyl which imparts the alcoholic character and that which imparts the acid character, both together furnish the elements which form the water given off.

Peculiar Anhydrides.—Lactic acid has the formula  $CH_3.CH\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.$. It contains an alcoholic hydroxyl and an acid hydroxyl. When the acid is distilled it loses water, and a compound of the formula  $CH_3.CH\left\langle\begin{matrix}\text{-O-}\\CO\end{matrix}\right\rangle$ is formed. This is lactic anhydride. As will be seen, the anhydride is formed by the loss of the elements of water from both hydroxyl groups together. Salicylic acid has the formula  $C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.$. It forms an anhydride in a similar manner, having the formula—
 $C_6H_4\left\langle\begin{matrix}\text{-O-}\\CO\end{matrix}\right\rangle$.

Substitution Products.

We have thus far considered the various classes of chemical compounds which are known to exist, and have shown that each class is characterized by some peculiarity of constitution which we recognize in each member of the class. There is in each compound a group which determines its character, making it an acid or an alcohol, an acetone or an aldehyde, etc. As long as this group remains unchanged, the compound belongs to the same class. If the group is changed, the compound loses its characteristics, and belongs to another class. On the other hand, the residues with which the class groups are united may undergo a variety of changes without interfering at all with the general properties of the compounds. The most common of these changes are those which are effected by substitution.

Chemical compounds act upon each other, in general, in two ways. 1st. They unite directly, forming only one product, as we see in the following reactions:—

$$\underset{\text{Ammonia.}}{NH_3} + HCl = \underset{\text{Ammonium chloride.}}{NH_4Cl}$$

$$\underset{\text{Ethylene.}}{C_2H_4} + Br_2 = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}$$

2d. They exchange certain constituents, forming two or more new products, thus:—

$$\underset{\text{Ethane.}}{C_2H_6} + Cl_2 = \underset{\text{Chlorethane.}}{C_2H_5Cl} + HCl$$

$$\underset{\text{Aldehyde.}}{CH_3.COH} + 6Cl = \underset{\text{Trichloraldehyde.}}{CCl_3.COH} + 3HCl$$

$$\underset{\text{Benzene.}}{C_6H_6} + H_2SO_4 = \underset{\text{Sulphobenzenic acid.}}{C_6H_5.SO_3H} + H_2O$$

$$\underset{\text{Benzene.}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5(NO_2)} + H_2O$$

The latter kind of action is by far the most common. It is that which is called substitution. In the above examples, the principal products are called substitution products, though, strictly speaking, both products are substitution products.

While the principle of substitution is recognized in connection with nearly all chemical reactions, and hence nearly all chemical compounds may be considered as substitution products with reference to some other compounds, still it is customary to include under this head only those products which are formed by the replacement of hydrogen in carbon compounds; and the substitutions which are spoken of are only those which can be actually effected—not imaginary cases.

Substitution Products containing Chlorine, Bromine, or Iodine.—The simplest examples of substitution products are those which are formed by the action of any of [illegible] carbon compounds. The [illegible] consists in the replacement of one or more atoms of hydrogen from the compound, and the filling of the places [illegible] by a corresponding number of atoms of the substituting element. The constitution of the products is the same as that of the compounds from which they are formed. Thus we have acetic acid, [illegible] chloracetic acids from it, the following reactions taking place successively:—

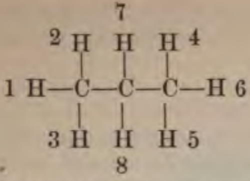
$CH_3.COOH + Cl_2 = CH_2Cl.COOH + HCl$
$CH_2Cl.COOH + Cl_2 = CHCl_2.COOH + HCl$
$CHCl_2.COOH + Cl_2 = CCl_3.COOH + HCl$

The constitution of these three different products is essentially the same as that of the acid from which they are derived.

Among these simple substitution products, however, differences are possible, and are actually observed, which are not possible in the original compounds. Take the hydrocarbon propane, C_3H_8. The constitution of this hydrocarbon is

$$\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ H & — & C & — & C & — & C — H \\ & & | & & | & & | \\ & & H & & H & & H \end{array}$$

The hydrogen atoms cannot be arranged in any other way with reference to the carbon atoms. There is but one hydrocarbon of this composition possible. But the carbon atoms in this compound differ from each other. The two which are represented as ending the chain in the formula are alike, while the central atom differs from them. The first are in combination with carbon by means of only one affinity each, while the central atom is joined to carbon by means of two affinities. We would naturally expect then that the difference between these two kinds of carbon atoms would cause a difference between the hydrogen atoms combined with them. If such a difference exists, then, different products must be obtained according as we replace a hydrogen atom attached to one of the terminal carbon atoms, or another hydrogen atom attached to the central carbon atom. Thus, if in the following formula—



$$\begin{array}{ccccccccc}
 & & & & 7 & & & & \\
 & & {}^{2}\mathrm{H} & & \mathrm{H} & & \mathrm{H}^{4} & & \\
 & & | & & | & & | & & \\
1\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H}\ 6 \\
 & & | & & | & & | & & \\
 & & 3\ \mathrm{H} & & \mathrm{H} & & \mathrm{H}\ 5 & & \\
 & & & & 8 & & & &
\end{array}$$

we replace any of the hydrogen atoms numbered 1, 2, 3, 4, 5, 6 by an element such as chlorine, the resulting compound would in each case be the same.

If, however, we replace one of the hydrogen atoms numered 7 or 8 by the same element, a compound of the same composition, but of different constitution, would be obtained. The formulas of the two compounds would be respectively

$$CH_2Cl\,CH_2.CH_3 \quad \text{and} \quad CH_3.CHCl.CH_3.$$

Thus we see that the position of a substituting element must be taken into consideration in studying the constitution of compounds. In connection with the individual compounds, which will be briefly considered in the last section of this book, the methods will be described which enable us to determine the positions of substituting elements and groups.

Complex Substitution Products.—Under this head we include all those products which are formed by replacing the hydrogen of a carbon compound either partially or wholly by groups. In accordance with what has just been said concerning the simple substitution products, it is plain that, in studying the constitution of the complex substitution products, two things must be taken into consideration:—

1st. The constitution of the substituting group itself, and,

2d. The position of the group in the molecule of the substitution product.

We shall here only take up the first part of the problem.

Constitution of Substituting Groups.—The groups which we shall have to consider are the following: The cyanogen group CN, and an isomeric group; the sulpho group SO_3H; the nitro group NO_2; the nitroso group

NO; the amido group NH_2; the imido group NH; and a few other groups intimately connected with those mentioned.

Constitution of the Group CN.—That acid of carbon which consists of a nitrogen atom and a hydrogen atom combined with a carbon atom, viz., hydrocyanic acid, has already been referred to. By appropriate reactions it is possible to transfer the group CN, contained in hydrocyanic acid, to other compounds in such a way that it takes the place of hydrogen, forming a substitution product. It is univalent, and hence its constitution is expressed by the formula $-C\equiv N$. We have the following reactions:—

$$\underset{\text{Monochloracetic acid.}}{CH_2Cl.COOH} + \underset{\text{Potassium cyanide.}}{KCN} = \underset{\text{Cyanacetic acid.}}{CH_2(CN).COOH} + KCl$$

$$\underset{\text{Ethylene bromide.}}{C_2H_4Br_2} + \underset{\text{Potassium cyanide.}}{2KCN} = \underset{\text{Ethylene cyanide.}}{C_2H_4(CN)_2} + 2KCl.$$

These substitution products, which consist only of the group $-C\equiv N$ combined with a hydrocarbon residue, are called *nitriles.*

A few other compounds are known which have the same composition as the nitriles, but a different constitution. They are known as *isonitriles* or *carbylamines.* They contain the group $C\equiv N-$. This group is univalent, just as the group $-C\equiv N$, but the nitrogen atom contained in it plays the part of a quinquivalent element, whereas, the nitrogen atom of the group $-C\equiv N$ is trivalent. We may have thus the two compounds—

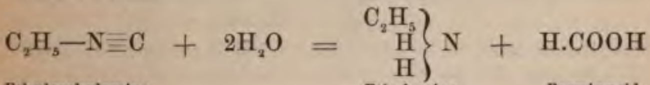
$$C_2H_5-C\equiv N \qquad \text{and} \qquad C\equiv N-C_2H_5,$$

of the same composition, but different constitution. Both these compounds are well known. The former is called ethyl cyanide or propionitrile, the latter ethylcarbylamine.

As ethyl cyanide, when treated with an alkali, yields propionic acid, we conclude that the carbon atom of the group CN is united directly with the hydrocarbon residue. For if it had not been, the removal of the nitrogen ought to have caused the formation of a product containing a smaller number of carbon atoms than the cyanide itself. The reaction which does actually take place is that which we have considered above as giving rise to the formation of acids from the cyanides, viz.:—

$$\underset{\text{Ethyl cyanide.}}{C_2H_5.CN} + 2H_2O = \underset{\text{Propionic acid.}}{C_2H_5.COOH} + NH_3$$

If the group CN had been in combination with the hydrocarbon residue by means of the nitrogen atom, which would be the case if the group had the constitution C≡N—, we should expect the nitrogen atom to remain in combination with the hydrocarbon residue, in case of decomposition, or we should expect the nitrogen atom to take with it the carbon atom with which it is most intimately combined. In either case, a separation of the carbon atoms would be the result, and we would obtain products containing a smaller number of carbon atoms than the original compound contained. This is exactly what takes place when the carbylamines are decomposed. When treated with hydrochloric acid they yield two products; one of these is formic acid, a compound containing one atom of carbon; the other consists of the hydrocarbon residue of the original compound combined with the nitrogen atom and hydrogen. Thus, in the case of ethylcarbylamine, the decomposition may be represented as follows:—

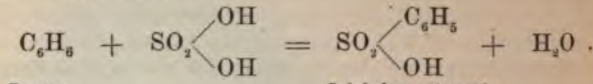


$$C_2H_5—N\equiv C + 2H_2O = \left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N + H.COOH$$

Ethylcarbylamine. Ethylamine. Formic acid.

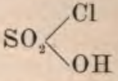
The fact that the compound $N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.$, in which the nitrogen atom is evidently in combination with the hydrocarbon residue, is so readily formed, leads us to the conclusion that in the original compound the same kind of union existed. The fact, also, that the one carbon atom is given off so readily from the molecule, indicates clearly that it was held in combination in some manner different from that in which the other carbon atoms of the molecule are held in combination. Taking the two facts and conclusions together, we are led to the formula above assigned to the carbylamine group, viz., C≡N— as the correct one.

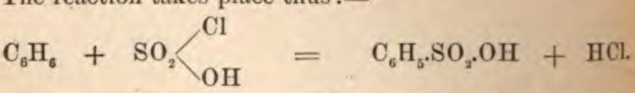
Constitution of the Group SO_3H.—By the action of concentrated sulphuric acid upon hydrocarbons and various other compounds containing hydrogen, derivatives are obtained which differ from the original compounds in containing the group SO_3H in the place of hydrogen. The reaction consists in the formation of water and the new derivative, thus:—



$$C_6H_6 + SO_2\left<\begin{matrix}OH\\OH\end{matrix}\right. = SO_2\left<\begin{matrix}C_6H_5\\OH\end{matrix}\right. + H_2O\,.$$

Benzene. **Sulphobenzenic acid.**

These products all act like acids in every way, so that we are justified in assuming the presence of hydroxyl in them. As they are formed so readily from sulphuric acid, it is also fair to assume that the group SO_2OH is a residue of sulphuric acid. Then, if we know the constitution of sulphuric acid, the constitution of this group will also be known to us. The fact that this group is a residue of sulphuric acid is shown also in the following way: By replacing one of the hydroxyl groups of sulphuric acid by an atom of chlorine, we obtain a compound of the formula  $SO_2\left<\begin{matrix}Cl\\OH\end{matrix}\right.$, which, by simple treatment with water, is reconverted into sulphuric acid. There can be no doubt that the group SO_2OH of this chloride has exactly the same constitution as the corresponding group of the acid. But, if this chloride be allowed to act upon benzene, sulphobenzenic acid and hydrochloric acid are the products, the former having all the properties possessed by the sulphobenzenic acid obtained from the action of sulphuric acid upon benzene. The reaction takes place thus:—



$$C_6H_6 + SO_2\left<\begin{matrix}Cl\\OH\end{matrix}\right. = C_6H_5.SO_2.OH + HCl.$$

Here, evidently, the group $SO_2.OH$ of the chloride takes the place of an atom of hydrogen in benzene.

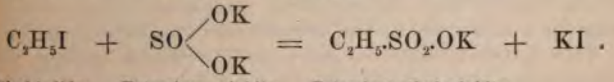
Assuming, then, the general formula $SO_2.OH$ for the group, it remains to decide in what manner the atoms of the sub-group SO_2 are united. If both sulphur and oxygen act as bivalent elements, two possibilities present themselves. We may have either —O—S—O— or —S—O—O—. If the former expresses the constitution of the group, then it is plain that the hydrocarbon must be united with it through the instrumentality of oxygen, whereas, if the latter is the correct expression, the hydrocarbon residue may be held in combination, either through the instrumentality of oxygen or sulphur. For, we may have either—

1, C_6H_5—O—O—S—OH ; or, 2, C_6H_5—S—O—O—OH.

Inasmuch as by reduction sulphydrates are obtained from the sulpho acids, it is believed that, in the latter, the grouping of the atoms is similar to that in the second of the above formulas. The sulphydrates have the general formula R(SH), in which R represents a hydrocarbon residue. This residue is united directly with the sulphur, and this in turn with the hydrogen. The proof of this constitution of the sulphydrates has been considered under the head of hydroxides.

Whenever then the group —S—O—O—OH enters into a compound in the place of a hydrogen atom, the resulting compound is a true sulpho acid.

Again, when a chloride, bromide, or iodide of a hydrocarbon or other residue is treated with an aqueous solution of a neutral sulphite, a derivative is obtained which has the same general composition as the sulpho acid, as may be seen in the following equation:—



$$C_2H_5I \;+\; SO\begin{cases}OK\\OK\end{cases} \;=\; C_2H_5.SO_2.OK \;+\; KI\;.$$

Ethyl iodide. Potassium sulphite. Potassium ethylsulphite.

These compounds were supposed to be identical with the sulpho acids. Indeed, in a few cases, it seems that the compounds obtained by this latter method must have the constitution above accepted for true sulpho acids. Nevertheless, it has recently been shown that the compounds obtained from the sulphites differ from true sulpho acids; that the former are really ethers of sulphurous acid, and not substitution products, in the sense in which we have here used that expression. The following experiments furnish the proofs :—

When benzylchloride, $C_6H_5.CH_2Cl$, is treated with potassium sulphite, reaction ensues in the manner above indicated, viz.:—

$$C_6H_5.CH_2Cl + K_2SO_3 = C_6H_5.CH_2.SO_3K + KCl.$$

When the new salt is treated with phosphorus chloride, the products of the reaction are phosphorus oxychloride, $POCl_3$, thionylchloride, $SOCl_2$, and benzylchloride, $C_6H_5.CH_2Cl$. If the salt had been derived from a true sulpho acid, a sulpho chloride of the formula $C_6H_5.CH_2.SO_2Cl$ would have been obtained. It is hence concluded that, in the salt, the sulphur does not hold the rest of the group in combination with the hydrocarbon residue, but that this is accomplished by means of an oxygen atom—the group having the constitution expressed by the formula

$$—O—S—O—O—H; \text{ or by } O—O—S—O—H.$$

The formation of the above products can then readily be explained:—

$$\begin{array}{l} C_6H_5.CH_2.O.S.O—OK \quad \text{yields} \\ C_6H_5.CH_2Cl \;\Big|\; Cl—S—O—Cl \;\Big|\; ClK. \end{array}$$

The oxygen abstracted will, of course, form phosphorus oxychloride. If sulphur had occupied either of the positions occupied by the oxygen atoms in the above formula which are abstracted, one of the products of the reaction would have been phosphorus sulphochloride, $PSCl_3$, whereas not a trace of this substance could be detected.

This subject requires more investigation before the conclusions above drawn can be looked upon as definitely settled. In all probability it will be found that there are, as stated, two isomeric groups, SO_3H, only one of which can give true sulpho acids. The formula above given for the sulpho-acid group will also probably be found to be the correct one. Further, from experiments thus far made, it seems more than likely that these groups easily undergo transformation, their atoms being rearranged.

Constitution of the Group NO_2.—When concentrated nitric acid is allowed to act upon hydrocarbons, etc., hydrogen is frequently replaced by the group NO_2, thus:—

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{NO_2OH} = \underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + H_2O.$$

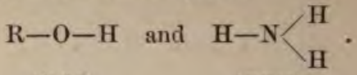
The reaction, as will be noticed, is similar to that which takes place when sulphuric instead of nitric acid is used. Just as in the former case we can assume that the group SO_3H is a residue of sulphuric acid, so in the latter case we can assume that the group NO_2 is a residue of nitric acid. The formula which we accept for nitric acid will show us the constitution of the group NO_2. Again, nitro compounds are formed by treating a chloride, bromide, or iodide of a hydrocarbon residue with silver nitrite, $AgNO_2$, the reaction taking place as follows:—

$$\underset{\text{Ethyl iodide.}}{C_2H_5I} + AgNO_2 = \underset{\text{Nitroethane.}}{C_2H_5(NO_2)} + AgI.$$

It would appear from the latter reaction that the group NO_2 has the same constitution in the nitro derivatives that it has in nitrous acid; but this is in reality not the case, or, at least, certain facts seem to indicate clearly a dissimilarity of the groups.

There are two series of compounds of the same composition, but of different constitution, both of which contain the group NO_2. The members of one of these series are ethers of nitrous acid. If nitrous acid contains hydroxyl, then the ethers would have the general constitution R—O—NO, in which R represents a hydrocarbon residue. The characterizing feature in the constitution of these ethers is the same as that which we find in all ethers, viz., the acid group is combined with the hydrocarbon residue by means of an *atom of oxygen*. That this is true of the ethers of nitrous acid is shown by the fact that, when nascent hydrogen acts upon them, they yield the alcohols corresponding to the hydrocarbon residues which they contain, and at the same time ammonia. If the nitrogen atom had been directly united with the hydrocarbon residue, we would have found it in combination with this residue after the above reduction. The decomposition which actually takes place may be represented thus:—

Ether, $R—O—N=O$ yields



$$R—O—H \quad \text{and} \quad H—N\begin{matrix} H \\ H \end{matrix} .$$

Alcohol. Ammonia.

With the constitution assumed for the ether, it is evident that the formation of alcohol by the addition of hydrogen would necessitate the splitting off of the group containing nitrogen.

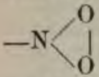
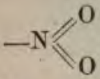
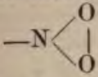
On the other hand, the second series of compounds are not ethers of any acid, but are true substitution products. They consist of a hydrocarbon residue combined with the group NO_2 by means of the *nitrogen atom.* Their general constitution is expressed by the formula $R—NO_2$.

This conclusion is reached by considering the products of the reduction of nitro compounds. When treated with nascent hydrogen, they yield products known as amine bases, which are ammonia in which one hydrogen atom has been replaced by a hydrocarbon residue. The decomposition is represented as follows:—

$$\underset{\text{Nitro products.}}{R—NO_2} + 6H = \underset{\text{Amine base.}}{R—NH_2} + 2H_2O.$$

In the product obtained in this case, it is evident that the nitrogen atom is in direct combination with the hydrocarbon residue, and hence we can assume that this kind of combination also existed in the original nitro compound.

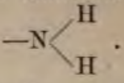
Accepting the above formula for nitro compounds, it is difficult to see how they can be formed by reaction with silver nitrite. For, if the hydrocarbon residue took the place occupied by the silver in the salt, it is plain that the product would be an ether which, according to what has already been said, must have the formula $R—O—NO$. The product, however, is not an ether. Consequently, some other change besides that of an interchange of places by the silver atom and the hydrocarbon residue must be accomplished at the same time. Consequently, further, the group NO_2 in nitrous acid has a constitution differing from that of the group NO_2 of nitro compounds.

As to the respective constitutions of these two groups we see that in nitrous acid we have in all probability one hydroxyl. This gives us one oxygen atom combined by one affinity with hydrogen, and, on the other side, with nitrogen, thus: H—O—N—. The only thing that is otherwise present in the molecule is an atom of oxygen which, it is safe to suppose, is combined by both its affinities with nitrogen; whence we have the group —O—N=O as the characteristic group of the acid and its derivatives. But the group of nitro compounds unites with residues by means of its nitrogen atom, as we have seen. Hence, we can conceive of two formulas for the group NO_2, viz.,  $-\mathrm{N}\left\langle\begin{array}{c}\mathrm{O}\\ |\\ \mathrm{O}\end{array}\right.$, in which the nitrogen is trivalent, and  $-\mathrm{N}\begin{array}{l}{=}\mathrm{O}\\ {=}\mathrm{O}\end{array}$, in which the nitrogen is quinquivalent. It has not been found possible to decide which of these two formulas is the correct one. The former,  $-\mathrm{N}\left\langle\begin{array}{c}\mathrm{O}\\ |\\ \mathrm{O}\end{array}\right.$, is now more commonly accepted than the latter. The fact that the group is so readily converted into the group NH_2, in which the nitrogen atom is undoubtedly trivalent, makes this formula appear probable.

Constitution of the Group NO.—A class of bodies which have recently been quite fully investigated contain the group NO in the place of hydrogen. They are known as *nitroso compounds.* Their preparation is accomplished by allowing the compound NOBr to act upon mercury derivatives of hydrocarbons, thus:—

$$Hg(C_6H_5)_2 + NOBr = Hg(C_6H_5)Br + C_6H_5(NO).$$

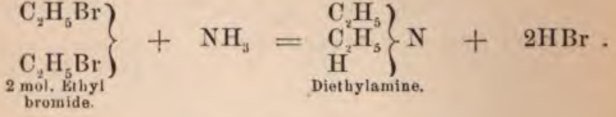
Assuming that nitrogen here acts as a trivalent element, and oxygen as bivalent, the constitution of the group NO can only be represented by the formula —N=O, according to which the combination between the hydrocarbon residue and the substituting group in nitroso compounds is accomplished by means of a nitrogen atom. This view, further, is in accordance with the fact that, by reduction, the group NO, like NO_2, is converted into NH_2.

Constitution of the Group NH_2.—Compounds which contain the group NH_2 are called *amido compounds*. The group is plainly a residue of ammonia and is univalent, having the constitution  $-N\begin{matrix}H\\H\end{matrix}$. These compounds are readily obtained by the action of nascent hydrogen on nitro derivatives, the group NO_2 being hereby converted into NH_2. Amido substitution products have properties which ally them to ammonia, which fact is a further evidence of a similarity in the constitutions of the two. They have basic properties in the same sense that ammonia has basic properties, *i. e.*, they unite directly with all acids forming salts. In addition to the above method of formation, we have also the action of aqueous ammonia upon chlorides, bromides, or iodides of hydrocarbon residues.

$$\underset{\text{Ethyl bromide.}}{C_2H_5Br} + NH_3 = \underset{\text{Ethylamine.}}{C_2H_5(NH_2)} + HBr.$$

This latter method indicates very decidedly the intimate connection between amido compounds and ammonia.

Constitution of the Group NH.—Finally, there are a few representatives known of a class of bodies called *imido compounds*. These contain the group NH, which is bivalent, and hence occupies the place of two hydrogen atoms. Like amido compounds, they may be considered as derived from ammonia by the replacement of two hydrogen atoms by hydrocarbon residues. The constitution of the group and of the compounds is readily understood. We have—



$$\underset{\substack{\text{2 mol. Ethyl}\\\text{bromide.}}}{\left.\begin{matrix}C_2H_5Br\\C_2H_5Br\end{matrix}\right\}} + NH_3 = \underset{\text{Diethylamine.}}{\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N} + 2HBr\ .$$

The various classes of chemical compounds which we have thus studied are the principal classes with which we have to deal. There are a few other classes, among which may be mentioned the so-called *mustard oils* and the *quinones*. These will be considered later, in connection with those better known compounds with which they are most closely allied.

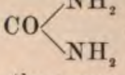
In classifying compounds we have distinguished between general classes and their substitution products. This distinction is generally justified, though, in a certain sense, even those compounds which belong to the general classes are substitution products, or, at least, may be considered as such. This is particularly the case with the compounds of carbon, all of which may be looked upon as derived from certain hydrocarbons by the replacement of something else. Thus the alcohols are derived from hydrocarbons by replacing hydrogen by hydroxyl, OH; the acids by replacing hydrogen by carboxyl, CO.OH, etc. Speaking, then, of all the groups which have been studied as substituting groups, the general statement may be made that: In all substituting groups the characterizing element or elements may be replaced by another or others of the same general character. Thus, as we have already seen, O may be replaced by S. Further, S may, in some cases, be replaced by Se or Te; N may be replaced by P, etc. Thus we get new compounds, but the constitution of these new compounds is the same as that of those from which they are derived, and hence they require no separate study in this place.

II.

SPECIAL STUDY OF THE CONSTITUTION OF CHEMICAL COMPOUNDS.

From the general considerations of the preceding section, the constitution of the majority of compounds will be directly understood. In the following section, the constitution of individual compounds will be considered, in so far as any special consideration of them is necessary. Here the compounds of carbon again will require most of our attention, because more is known concerning their constitution than is known concerning other compounds. It will be found that the same atoms may frequently be arranged in different ways, giving rise to different compounds.

Isomerism.—There are two ways in which bodies may contain the same elements in the same proportions by weight, and still be different bodies:—

1. The atoms or groups composing the body may be arranged differently in the molecule, as above stated. Thus we have ammonium cyanate, $CN(ONH_4)$, and urea or carbamide,  $CO\begin{cases} NH_2 \\ NH_2 \end{cases}$. These bodies contain the same atoms in the same number in their molecules. Such bodies are called *metameric.*

2. Bodies may have the same composition, but have different molecular weights. Thus we have acetylene, C_2H_2, and benzene, C_6H_6. Such bodies are called *polymeric.*

Compounds not Containing Carbon.

The compounds which the monovalent elements, hydrogen, chlorine, bromine, iodine, fluorine, sodium, potassium, lithium, cæsium, rubidium, silver, form with each other have the simplest constitution of which we have any conception. They require no study here.

Compounds of Chlorine, etc., with Oxygen, and Oxygen and Hydrogen.—Hydrogen peroxide has the empirical formula H_2O_2. If in this compound the oxygen is bivalent, the arrangement of the atoms can be most readily imagined to be in accordance with the formula $\mathrm{H-O-O-H}$. There is, indeed, no independent proof of the correctness of this formula, but no other formula expresses the constitution at all satisfactorily, and hence this is accepted as correct.

The acids which chlorine forms with oxygen and hydrogen are most frequently considered as represented by the following formulas:—

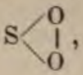
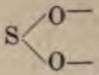
$\mathrm{Cl-O-H}$,	hypochlorous acid,
$\mathrm{Cl-O-O-H}$,	chlorous acid,
$\mathrm{Cl-O-O-O-H}$,	chloric acid,
$\mathrm{Cl-O-O-O-O-H}$,	perchloric acid;

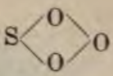
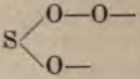
and the compounds of chlorine with oxygen alone by the following formulas:—

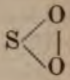
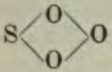
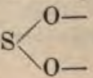
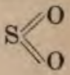
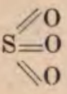
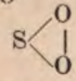
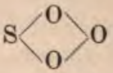
$\mathrm{Cl-O-Cl}$,	hypochlorous anhydride,
$\mathrm{Cl-O-O-O-Cl}$,	chlorous anhydride,
$\mathrm{Cl-O-O-O-O-Cl}$,	chlorous-chloric anhydride.

The corresponding compounds of bromine, iodine, and fluorine, as far as they are known, are represented by corresponding formulas. It must be confessed that these formulas are by no means well established, and it is very possible that, when the compounds themselves shall have been studied more carefully, they will be found to be incorrect.

Compounds of Sulphur, etc., with Oxygen, and Oxygen and Hydrogen.—Sulphur forms a number of compounds with oxygen, and with oxygen and hydrogen, some of which have been carefully studied. The compounds with oxygen alone are sulphur dioxide, SO_2, and sulphur trioxide, SO_3. If in these compounds both the sulphur and the oxygen are bivalent, we have the following possible formulas:—

For SO_2, , , —S—O—O— ;

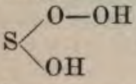
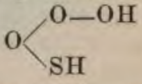
For SO_3, , , —S—O—O—O—.

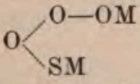
As is plain, all the formulas except  and  represent the compounds as unsaturated. Now SO_2 conducts itself like an unsaturated compound; it combines directly with chlorine, forming the product SO_2Cl_2, and with oxygen, forming SO_3, so that it seems possible that the formula  or —S—O—O— may in reality express its constitution. Again, some chemists consider sulphur quadrivalent or sexivalent in these compounds, which would give the formulas  and . Perhaps the most commonly accepted formulas are  and , though the reasons for accepting them are not very good ones.

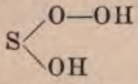
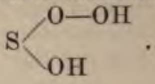
The acids of sulphur are the following:—

H_2SO_3,	sulphurous acid.
H_2SO_4,	sulphuric acid.
$H_2S_2O_7$,	pyrosulphuric acid.
$H_2S_2O_3$,	hyposulphurous or thiosulphuric acid.
$H_2S_2O_6$,	hyposulphuric or dithionic acid.
$H_2S_3O_6$,	trithionic acid.
$H_2S_4O_6$,	tetrathionic acid.
$H_2S_5O_6$,	pentathionic acid.

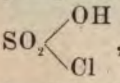
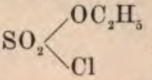
Sulphurous Acid, H_2SO_3.—Only derivatives of this acid are known—as the salts and ethers. From a study of these derivatives, conclusions have been drawn concerning the constitution of the acid itself. The constitution of sulphurous acid is expressed by very different formulas by those who consider sulphur as bivalent, and those who consider that it may and does act as quadrivalent or sexivalent. Up to the present, no conclusive evidence of either view has been furnished. We propose to consider sulphur as bivalent, and to show to what conclusions we shall then be led. This we can do without interfering with our main object, which is to show more particularly the methods of thought and experiment that lie at the foundation of constitutional formulas in general.

If then sulphur is bivalent, we have as probable formulas for sulphurous acid  $S\left\langle\begin{matrix}O-OH\\OH\end{matrix}\right.$ or  $O\left\langle\begin{matrix}O-OH\\SH\end{matrix}\right.$.

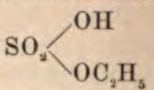
For some time the latter formula was accepted, in consequence of the fact that the sulpho acids are so readily formed from salts of sulphurous acid. We have seen that, in the sulpho acids, the group SO_3H is combined with hydrocarbon residues by means of the sulphur atom Now, as the group SO_3H can apparently be obtained from sulphites, such a constitution was assigned to the latter as to make the connection between them and the sulpho acids clear. This can best be accomplished if we accept the formula  $O\left\langle\begin{matrix}O-OM\\SM\end{matrix}\right.$ for the sulphites.

If the metal which is in combination with sulphur in this formula be replaced by a hydrocarbon residue, the latter would be in combination with sulphur also. On the other hand, if we accept the former of the two formulas above proposed, viz.,  $S\left\langle\begin{matrix}O-OH\\OH\end{matrix}\right.$, it would appear difficult to obtain sulpho acids from sulphites by a simple interchange of atoms or groups. Recent experiments seem to show that the compounds obtained from the sulphites, which were formerly looked upon as sulpho acids, are in reality ethers of sulphurous acid, and not sulpho acids; that in them, further, the hydrocarbon residue is not in combination with sulphur (see *ante*, p. 155). From this it is concluded that the formula of sulphurous acid is  $\mathrm{S}\left\langle\begin{matrix}\mathrm{O{-}OH}\\ \mathrm{OH}\end{matrix}\right.$.

Sulphuric Acid, H_2SO_4.—The same reasons which lead us to accept the formula —S—O—O—OH for the characterizing group of sulpho acids (see *ante*, p. 156), also lead us to accept this formula as part of the whole formula of sulphuric acid. But we know that sulphuric acid contains two hydroxyl groups, consequently, adding one hydroxyl group to the above group, we have as the formula for sulphuric acid, HO—S—O—O—OH.

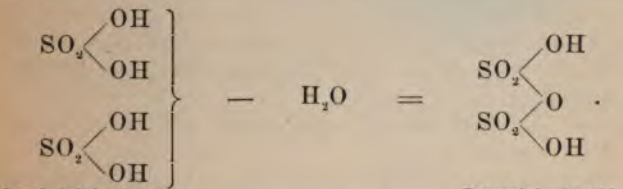
Another reason for accepting this formula is found in the following facts: By the action of the chloride of phosphorus on sulphuric acid, sulphuryl oxychloride,  $\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{Cl}\end{matrix}\right.$, is obtained. In this compound the chlorine in all probability occupies the place which, in sulphuric acid, is occupied by hydroxyl. This appears still more probable when we consider that the oxychloride is converted into the acid by simple treatment with water. Now, if sulphuryl oxychloride is treated with ethylene, a compound,  $\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{Cl}\end{matrix}\right.$, is formed by direct addition. Three formulas are possible for this compound, viz.:—

C_2H_5—O—O—S—O—Cl;
C_2H_5—O—S—O—O—Cl;
Cl—S—O—O—O—C_2H_5.

Further, if sulphuryl oxychloride is treated with alcohol it yields ethylsulphuric acid,  $\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OC_2H_5}\end{matrix}\right.$. If the formula of sulphuric acid were symmetrical—

HO—O—S—O—OH, then ethylsulphuric acid would be C_2H_5.O—O—S—O—OH, and a chloride derived from it would be C_2H_5.O—O—S—O—Cl. Sulphuryl oxychloride would have the formula HO—O—S—O—Cl, and the compound derived from it by the addition of ethylene would be C_2H_5.O—O—S—O—Cl; or this latter would be identical with the chloride of ethylsulphuric acid. The two are, however, not identical, and hence it follows that the formula of sulphuric acid cannot be symmetrical, thus, HO—O—S—O—OH. If it is not symmetrical, however, it must be HO—S—O—O—OH.

Pyrosulphuric Acid, $H_2S_2O_7$.—Pyrosulphuric acid is a partial anhydride of sulphuric acid obtained by abstracting one molecule of water from two molecules of the acid:—

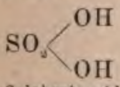


$$\left.\begin{array}{l} SO_2{<}^{OH}_{OH} \\ SO_2{<}^{OH}_{OH} \end{array}\right\} - H_2O = \begin{array}{l} SO_2{<}^{OH} \\ \quad\;\; {>}O \\ SO_2{<}_{OH} \end{array}.$$

2 mol. Sulphuric acid. Pyrosulphuric acid.

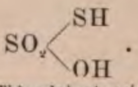
The general statements made in connection with the subject of anhydrides contain the proofs for the above formula. Of course, the groups SO_2 contained in this anhydride are supposed to have the same constitution that they have in sulphuric acid.

Hyposulphurous or Thiosulphuric Acid, H_2S_2O.—This acid is usually considered as sulphuric acid, in which one of the hydroxyl groups has been replaced by the sulphuryl group SH, thus:—



$$SO_2{<}^{OH}_{OH}$$

Sulphuric acid.

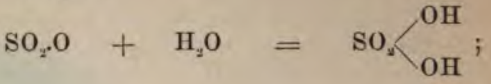


$$SO_2{<}^{SH}_{OH}.$$

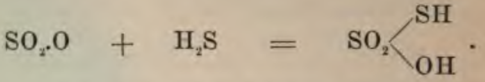
Thiosulphuric acid.

This formula is rendered probable by the fact that thiosulphuric acid may be obtained from sulphuric acid by treating the latter with phosphorus sulphide. The action of the latter reagent consists in replacing oxygen by sulphur. And the oxygen of the hydroxyl group is, in general, more susceptible to the influence of reagents than that contained in the group SO_2.

Further, thiosulphuric acid is obtained by allowing hydrogen sulphide to act upon sulphur trioxide, just as sulphuric acid is obtained by allowing water to act upon sulphur trioxide.

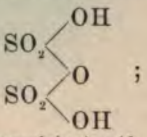


$$SO_2.O \quad + \quad H_2O \quad = \quad SO_2\begin{array}{l}OH\\OH\end{array};$$



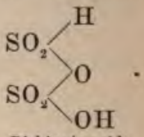
$$SO_2.O \quad + \quad H_2S \quad = \quad SO_2\begin{array}{l}SH\\OH\end{array}.$$

Other Polythionic Acids.—Dithionic acid, $H_2S_2O_6$, is considered as related to pyrosulphuric acid, thus:—



$$\begin{array}{l}SO_2\begin{array}{l}OH\\ \\ \end{array}\\ \qquad O\\ SO_2\begin{array}{l}\\ OH\end{array}\end{array};$$

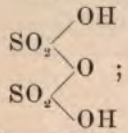
Pyrosulphuric acid.



$$\begin{array}{l}SO_2\begin{array}{l}H\\ \\ \end{array}\\ \qquad O\\ SO_2\begin{array}{l}\\ OH\end{array}\end{array}.$$

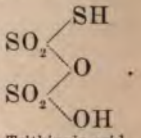
Dithionic acid.

Trithionic Acid, $H_2S_3O_6$, may be considered as derived from pyrosulphuric acid in the same way that thiosulphuric acid is derived from sulphuric acid, thus:—



$$\begin{array}{l}SO_2\begin{array}{l}OH\\ \\ \end{array}\\ \qquad O\\ SO_2\begin{array}{l}\\ OH\end{array}\end{array};$$

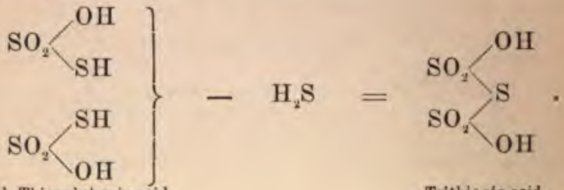
Pyrosulphuric acid.



$$\begin{array}{l}SO_2\begin{array}{l}SH\\ \\ \end{array}\\ \qquad O\\ SO_2\begin{array}{l}\\ OH\end{array}\end{array}.$$

Trithionic acid.

Or, it may be that trithionic acid is an anhydride of thiosulphuric acid:—

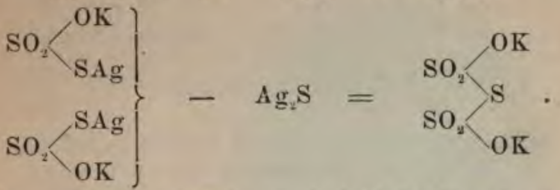


$$\left.\begin{array}{l}SO_2\begin{array}{l}OH\\SH\end{array}\\ \\ SO_2\begin{array}{l}SH\\OH\end{array}\end{array}\right\} - H_2S = \begin{array}{l}SO_2\begin{array}{l}OH\\ \\ \end{array}\\ \qquad S\\ SO_2\begin{array}{l}\\ OH\end{array}\end{array}.$$

2 mol. Thiosulphuric acid. Trithionic acid.

The latter view is rendered probable by the fact that trithionates are formed when double salts of thiosulphuric acid are boiled with water. The reaction takes place according to the following equation :—

$$2AgKS_2O_3 \quad = \quad Ag_2S \quad + \quad K_2S_3O_6.$$

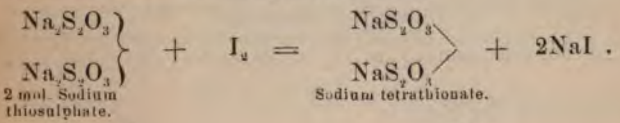


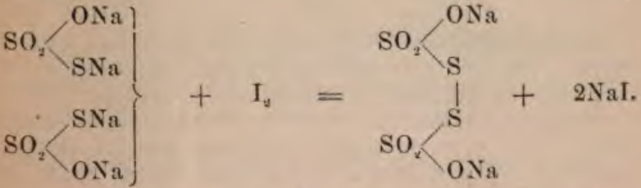
When potassium trithionate is boiled with potassium sulphide, potassium thiosulphate is formed—

$$K_2S_3O_6 \quad + \quad K_2S \quad = \quad 2K_2S_2O_3.$$

This reaction also indicates an intimate relation between thiosulphuric and trithionic acids.

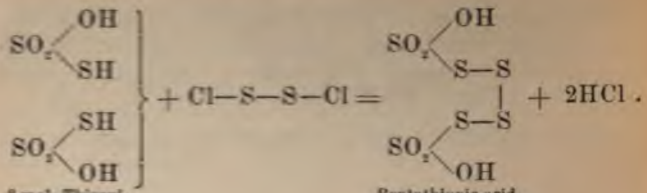
Tetrathionic Acid, $H_2S_4O_6$, is obtained by the action of iodine on sodium thiosulphate, thus:—





Hence, the formula of the acid from which the latter salt is derived is accepted for tetrathionic acid.

Pentathionic Acid, $H_2S_5O_6$, is obtained by treating barium thiosulphate with sulphur bichloride S_2Cl_2. The latter compound has the constitution Cl—S—S—Cl; consequently, the reaction may be interpreted most readily as follows :—



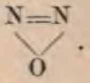
2 mol. Thiosulphuric acid.

Pentathionic acid.

The corresponding acids of selenium and tellurium, as far as they are known, are represented by similar formulas.

Compounds of Nitrogen with Oxygen, and with Oxygen and Hydrogen.—Nitrogen forms with oxygen the following compounds:—

N_2O,	nitrous oxide or nitrogen monoxide.
NO or N_2O_2,	nitrogen dioxide.
N_2O_3,	nitrogen trioxide.
NO_2 or N_2O_4,	nitrogen tetroxide.
N_2O_5,	nitrogen pentoxide.

The constitution of *nitrogen monoxide* is usually expressed by the formula  .

Nitrogen dioxide is $—N{=}O$, and is, therefore, unsaturated. The readiness with which it combines with oxygen and chlorine indicates its unsaturated condition.

Nitrogen tetroxide is $—O—N{=}O$, and is also unsaturated. This formula is given the compound because it is obtained so easily from the monoxide, and is converted into the latter so easily.

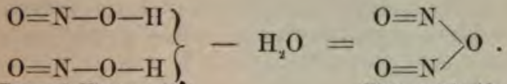
Nitrogen trioxide is the anhydride of nitrous acid. Hence its formula depends upon that of nitrous acid (which see).

Nitrogen pentoxide is the anhydride of nitric acid. Its formula depends upon that of nitric acid (which see).

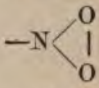
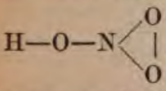
There are two acids of nitrogen, viz.:—

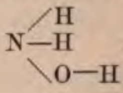
HNO_2,	nitrous acid.
HNO_3,	nitric acid.

Nitrous Acid, HNO_2.—The proofs for the presence of the group $—O—N=O$ in nitrous acid have been given under the head of nitro compounds (which see). The acid has the constitution $H—O—N=O$. From this formula we derive that of the anhydride, nitrogen trioxide, thus:—



Two mol. Nitrous acid. Nitrogen trioxide.

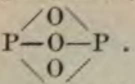
Nitric Acid, HNO_3.—It has been shown above (see Nitro Compounds) that the group contained in nitro compounds has probably the constitution . It being further probable that this group is contained in nitric acid, the constitution of the latter would be . The fact, that nitric acid is so volatile, seems to indicate that the nitrogen contained in it is trivalent rather than quinquivalent. We saw above other facts indicating the same thing, so that now the above formula is pretty generally accepted.

Hydroxylamine, H_3NO.—This substance is a strong base conducting itself like ammonia. By appropriate reactions it can be shown that two of the hydrogen atoms contained in the compound differ from the other one. These facts prove that hydroxylamine is a derivative of ammonia, and the formula is consequently .

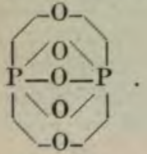
Compounds of Phosphorus with Oxygen, and with Oxygen and Hydrogen.—Phosphorus forms two oxides, viz.:—

P_2O_3,	phosphorus trioxide.
P_2O_5,	phosphorus pentoxide.

The former is usually considered as derived from trivalent phosphorus, and to it is consequently given the formula



The latter, however, is considered as derived from quinquivalent phosphorus, and to it is given the formula

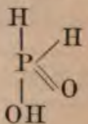


These formulas are purely hypothetical.

There are several acids of phosphorus, viz.:—

H_3PO_2,	hypophosphorous acid.
H_3PO_3,	phosphorous acid.
H_3PO_4,	phosphoric acid.
$H_4P_2O_7$,	pyrophosphoric acid.
HPO_3,	metaphosphoric acid.

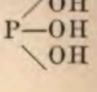
Hypophosphorous acid, H_3PO_2, is monobasic, and hence only one hydroxyl group is assumed as present in its molecule. This gives the formula $H_2PO.OH$ or



$$\text{P}(\text{H})(\text{H})(=\text{O})(\text{OH})$$

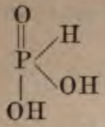
, in which the phosphorus atom is quinquivalent.

Phosphorous Acid, H_3PO_3.—In regard to the constitution of this acid, two views are held. According to the first, the formula of the acid is



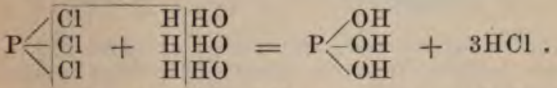
$$\text{P}(\text{OH})_3$$

, the phosphorus being trivalent. According to the second, the formula is



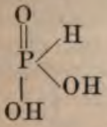
$$\overset{\displaystyle \mathrm{O}}{\overset{\|}{\underset{\underset{\displaystyle \mathrm{OH}}{|}}{\mathrm{P}}}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{OH}\end{matrix}\right.,$$

the phosphorus being quinquivalent. If the former formula is correct, the acid ought to be tribasic. In most of its salts, however, it is only bibasic. Still ethers are known which are evidently derived from a tribasic acid, as, for instance, $PO_3(C_2H_5)_3$; and it has, further, recently been shown that a salt of the acid exists in which there are three atoms of a monovalent metal to the molecule. These latter facts would lead to the formula $P(OH)_3$. The fact, also, that phosphorous acid is produced by simply treating phosphorus trichloride with water, is in accordance with this formula. We have



$$\mathrm{P}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right. + \begin{matrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\left|\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\\ \mathrm{HO}\end{matrix}\right. = \mathrm{P}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. + 3\mathrm{HCl}.$$

On the other hand, the following facts speak for the formula



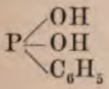
$$\overset{\displaystyle \mathrm{O}}{\overset{\|}{\underset{\underset{\displaystyle \mathrm{OH}}{|}}{\mathrm{P}}}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{OH}\end{matrix}\right. :—$$

When benzene is treated with phosphorus trichloride, under appropriate conditions, the following reaction takes place:—

$$PCl_3 + C_6H_6 = PCl_2(C_6H_5) + HCl.$$

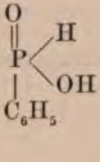
When the main product, phosphenyl chloride, is treated with water, the chlorine is eliminated, and a compound of the composition $PO_2H_2(C_6H_5)$ is formed. The formula of this compound may be either—

1,



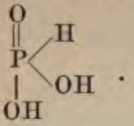
$$\mathrm{P}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{C_6H_5}\end{matrix}\right. ;$$

or, 2,



$$\overset{\displaystyle \mathrm{O}}{\overset{\|}{\underset{\underset{\displaystyle \mathrm{C_6H_5}}{|}}{\mathrm{P}}}}\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{OH}\end{matrix}\right. .$$

If the latter is the formula, then we can conclude that the constitution of phosphorous acid is similar, *i.e.*,



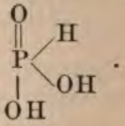
If formula 1 is correct, then by the action of phosphorus pentachloride upon the compound the following reaction ought to take place:—

I. $P(OH)_2C_6H_5 + 2PCl_5 = PCl_2(C_6H_5) + 2(POCl_3) + 2HCl.$

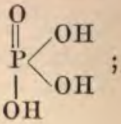
If, however, formula 2 is correct, then under the same conditions the following reaction would take place:—

II. $OPH(OH)C_6H_5 + 2PCl_5 = OPCl_2\,(C_6H_5) + POCl_3 + PCl_3 + 2HCl.$

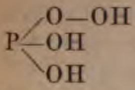
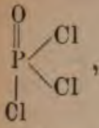
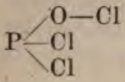
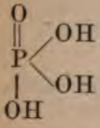
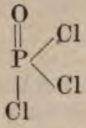
In the former case, phosphenyl chloride, $PCl_2(C_6H_5)$, would be formed; in the latter, phosphenyl oxychloride, $POCl_2(C_6H_5)$. Direct experiments showed that phosphenyl oxychloride, phosphorus oxychloride, and phosphorus trichloride are formed, and consequently the formula $OPH\ (OH)C_6H_5$ is correct; and phosphorous acid by analogy is $OPH(OH)_2$ or



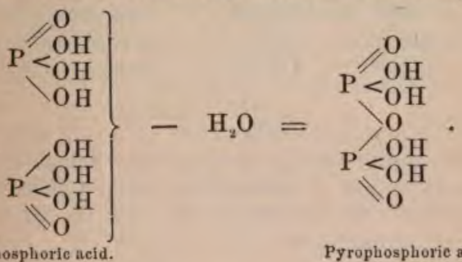
Phosphoric Acid, H_3PO_4.—This acid is tribasic, and hence three hydroxyl groups are assumed to be present in it. From this follows directly the formula $PO(OH)_3$. The question still remains whether the phosphorus is quinquivalent or trivalent in the latter. In the former case, the formula would be



in the latter,

 . Phosphoric acid is obtained by treating phosphorus oxychloride with water. If the oxychloride is  , then we would expect phosphoric acid to have the former of the two formulas given. If the oxychloride is  , then the acid has probably the latter of the two formulas given. The formulas  and  are usually accepted, though without positive proofs of their correctness.

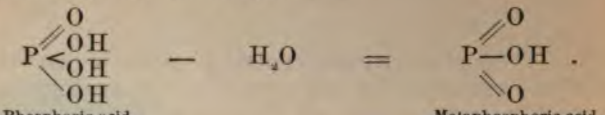
Pyrophosphoric Acid, $H_4P_2O_7$.—This is a partial anhydride of phosphoric acid formed by abstracting one molecule of water from two molecules of the acid, thus:—



2 mol. Phosphoric acid. Pyrophosphoric acid.

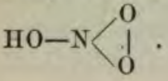
The constitution is readily understood by the aid of the general remarks on the subject of anhydrides.

Metaphosphoric Acid, HPO_3.—This acid has a composition analogous to that of nitric acid, HNO_3. It is, like pyrophosphoric acid, a partial anhydride of phosphoric acid, formed by abstracting one molecule of water from one molecule of the acid, thus:—



Phosphoric acid. Metaphosphoric acid.

Accepting the formula for phosphoric acid which is employed in this equation, the constitution of metaphosphoric acid would be that which is expressed. Nitric acid, it will be remembered, has probably the constitution



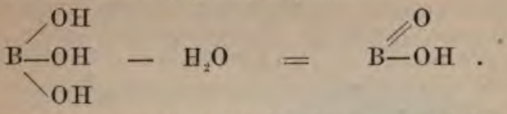
The relations between phosphoric acid and its anhydrides are shown by the following tables:—

$2(H_3PO_4) - H_2O = H_4P_2O_7$, pyrophosphoric acid.
$2(H_3PO_4) - 2H_2O = 2HPO_3$, metaphosphoric acid.
$2(H_3PO_4) - 3H_2O = P_2O_5$, phosphoric anhydride.

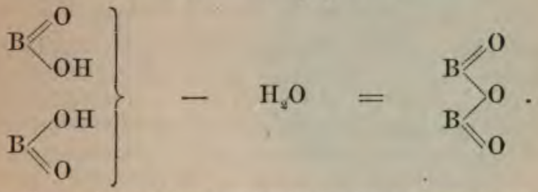
$P_2O_5 + H_2O = 2HPO_3$, metaphosphoric acid.
$P_2O_5 + 2H_2O = H_4P_2O_7$, pyrophosphoric acid.
$P_2O_5 + 3H_2O = 2H_3PO_4$, phosphoric acid.

Arsenic, antimony, and bismuth form some compounds analogous to those of phosphorus here described. What has been said of the constitution of the latter holds good of the constitution of the former.

Compounds of Boron with Oxygen and with Oxygen and Hydrogen.—Boron forms only one oxide, viz., B_2O_3, known as boron trioxide. The acid to which it corresponds is $B(OH)_3$. When boric acid, $B(OH)_3$, is heated for some time at 100° it loses a molecule of water, a partial anhydride being formed, thus:—



When this anhydride is heated to a much higher temperature, it is converted into B_2O_3, thus:—



The formulas of these anhydrides here given are purely hypothetical.

Compounds of Silicon with Oxygen and with Oxygen and Hydrogen.—Silicon bears a close analogy to carbon in some respects. It usually acts as a quadrivalent element, as is seen in the compound SCl_4. When this chloride is treated with water, we should expect as a product $Si(OH)_4$, which may be considered as the normal acid of silicon. It appears to be possible to obtain this acid, but it is very unstable. It loses water easily, and thus yields a partial anhydride, SiO_3H_2, thus:—

$$Si(OH)_4 \;-\; H_2O \;=\; SiO_3H_2 \;=\; SiO(OH)_2.$$

This compound is usually called silicic acid, as from it are derived most of the silicates.

If heated, this acid yields complicated polysilicic acids, which, in their turn, are partial anhydrides. They are formed by the union of two or more molecules of silicic acid and the abstraction of varying amounts of water from them. Examples of such polysilicic acids are—

$$Si_2O_3(OH)_2,\ Si_3O_4(OH)_4,\ Si_3O_5(OH)_2,\ Si_4O_7(OH)_2, \text{ etc.,}$$

some of which are found in nature, as opal, hydrophane, etc. As final product of the action of heat on silicic acid, we have silicon dioxide, SiO_2.

Salts.—The constitution of the most important acids being thus understood, that of the salts, in general, requires no special consideration; for we have seen that the salts are very simple derivatives of the acids. There are a few metals and groups, however, which have the property of yielding peculiar salts, and these require a brief consideration.

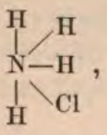
Ammonium Salts.—When ammonia, NH_3, acts upon any acid, a salt is formed by direct addition, thus:—

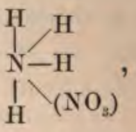
$$NH_3 + HCl = \underset{\text{Ammonium chloride.}}{(NH_4)Cl}$$

$$NH_3 + HNO_3 = \underset{\text{Ammonium nitrate.}}{(NH_4)NO_3}$$

$$2NH_3 + H_2SO_4 = \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4.}$$

The salts thus formed are similar to the salts of potassium, sodium, etc., KCl, KNO_3 K_2SO_4, etc. They conduct themselves like true metallic salts. Hence, the group NH_4, which is contained in them, is supposed to play the part of a metal, and to it the name ammonium is given. Accordingly, the salts are called ammonium salts. These have been referred to incidentally under the head of valence. It was shown that in them the nitrogen is quinquivalent. The formulas of the above salts are, accordingly—





etc.

Salts of Copper and Mercury.—Copper and mercury form two series of salts, of which the following are examples:—

Cu_2Cl_2, $CuCl_2$ | Hg_2Cl_2, $HgCl_2$
$Cu_2(NO_3)_2$, $Cu(NO_3)_2$ | $Hg_2(NO_3)_2$, $Hg(NO_3)_2$
$Cu_2(SO_4)$, $Cu(SO_4)$ | $Hg_2(SO_4)$, $Hg(SO_4)$.

If we determine the formulas of the two chlorides of mercury by the aid of the specific gravity of their vapors, we are led to HgCl and $HgCl_2$. According to these formulas, mercury is bivalent and the compound HgCl is unsaturated. It has been supposed, however, that the formula of the chloride HgCl in the solid condition is in reality Hg_2Cl_2, and that it has the constitution $\begin{array}{c} HgCl \\ | \\ HgCl \end{array}$.

The group $\begin{array}{c} Hg \\ | \\ Hg \end{array}$ is bivalent as well as the mercury atom itself, and thus the above two series of salts are explained. The same explanation is given for the *corresponding salts of copper.*

A large number of compounds are known which are derived from salts of ammonium and contain copper and mercury. They seem to consist of ammonium salts, in which a portion of the hydrogen of the ammonium groups has been replaced by copper or mercury, thus:—

$$Hg_2Cl_2 + 2NH_3 = \begin{array}{c} NH_3 \\ NH_3 \end{array} Hg_2 \begin{array}{c} Cl \\ Cl \end{array},$$ Dimercury diamido-chloride.

$NO_3.NH_2Hg_2$, Dimercuryamine nitrate.

These formulas are purely hypothetical.

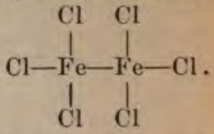
Similar compounds are formed with other metals, particularly with cobalt, which furnishes a very large number of interesting substances of this kind. These are too complicated and too little understood to permit the drawing of positive conclusions concerning their constitution. Their study promises important results.

Salts of Iron and Chromium.—Iron and chromium form two series of salts, as follows:—

$FeCl_2$,	$FeCl_3$,	or Fe_2Cl_6.
$Fe(NO_3)_2$,	$Fe(NO_3)_3$,	or $Fe_2(NO_3)_6$.
$FeSO_4$,	$Fe_2(SO_4)_3$.	
$CrCl_2$,	$CrCl_3$,	or Cr_2Cl_6.
$Cr(NO_3)_2$,	$Cr(NO_3)_3$,	or $Cr_2(NO_3)_6$.
$CrSO_4$,	$Cr_2(SO_4)_3$.	

In regard to the formula of the second chloride of iron above represented by $FeCl_3$ or Fe_2Cl_6, there is still doubt.

A determination of the specific gravity of its vapor led to the formula Fe_2Cl_6, whereas a determination of the specific gravity of certain other derivatives of the same constitution as the chloride led to the simpler formula. If $FeCl_3$ is correct, the iron atom in the compounds corresponding to this chloride is trivalent, whereas, if Fe_2Cl_6 is correct, the iron atom is probably quadrivalent, and the constitution of the compound is



$$\mathrm{Cl}-\overset{\overset{\mathrm{Cl}}{|}}{\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{Fe}}}-\overset{\overset{\mathrm{Cl}}{|}}{\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{Fe}}}-\mathrm{Cl}.$$

Of course, the formulas for the salts of iron will depend upon those which we accept for the two chlorides. It is most commonly considered that iron may be bivalent or quadrivalent.

The salts of manganese resemble those of iron and chromium.

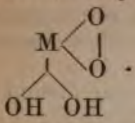
Salts of Aluminium.—The determinations which leave us in doubt concerning the formula of the higher chloride of iron also leave us in doubt concerning the formula of the chloride of aluminium. It is either $AlCl_3$ or Al_2Cl_6, and aluminium is either trivalent or quadrivalent.

Metal Acids.—The four metals, iron, chromium, manganese, and aluminium, form hydroxides of the general formula MO.OH, which conduct themselves like weak acids, forming salts with some metals. Thus, we have AlO.OK and AlO.ONa, salts of the hydroxide AlO.OH.*

Iron, manganese, and chromium yield acids of the general formula MO_4H_2. Thus we have FeO_4H_2, MnO_4H_2, and CrO_4H_2. These acids are analogous to sulphuric acid $H\ SO_4$, and a close resemblance is noticed between the salts of sulphuric acid and those of chromic acid, which is the best known of the three above-named acids.

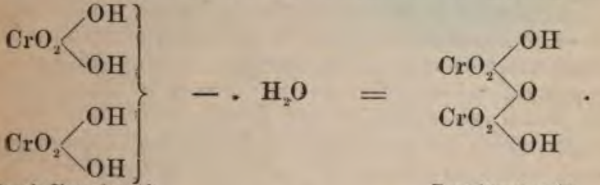
* Of course, if the chloride is Al_2Cl_6, this compound is $Al_2O_2(OH)_2$, and the salts have a corresponding composition.

If the metals are quadrivalent in these acids, their constitution may be expressed by the general formula—



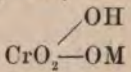
If they are bivalent, their constitution would be similar to that of sulphuric acid. As far as the evidence thus far in our possession is concerned, we are as much justified in accepting one of these formulas as the other.

A very important salt of chromium is that known as potassium bichromate. The formula of this salt is $Cr_2O_7K_2$. It may be regarded as the salt of an acid which is analogous to pyrosulphuric acid and derived from chromic acid by the abstraction of water, thus:—



2 mol. Chromic acid. Pyrochromic acid.

Neither chromic acid itself nor pyrochromic acid can be prepared in the free condition. The group CrO_2 does not appear to be capable of holding hydroxyl in combination. So that salts of the formula



$CrO_2\begin{matrix}-OH\\-OM\end{matrix}$

are not known.

An acid of manganese furnishes salts of the general formula MnO_4M. No positive assertion can be made in regard to the constitution of this acid, except that it is monobasic, and hence it probably contains one hydroxyl group. This gives the formula $MnO_3—OH$, but the group MnO_3 remains unexplained.

Compounds of Uranium.—In connection with the subject of bases it was mentioned that uranium forms a peculiar set of salts in which the monovalent group UO takes the place of the hydrogen of the acids. This group UO is, like U itself, a base residue, and hence, according to the general definition of salts, it may take the place of hydrogen in the acids, and the resulting compounds will be just as strictly salts as those compounds in which the base residue consists of a metal alone.

Uranium, further, forms salts of the general formula $U_4O_7M_2$, which may be supposed to be derived from a complex hydroxide, $U_4O_7H_2 = OU.O.U(OH).O.UO$. This formula is, however, only hypothetical.

CONSTITUTION OF CARBON COMPOUNDS.

As has already been intimated, a great deal more is known concerning the constitution of carbon compounds than is known concerning the constitution of those compounds which do not contain carbon. Having considered the general constitution of the classes of compounds with which we meet, it only remains to study those changes which the members of the different classes can undergo without losing their main characteristics. We shall find that the compounds of carbon may be divided into a few distinct groups; that each of these groups possesses a mother-substance from which all the other members of the group may be derived. The principal groups are: the Marsh-gas, or Methane compounds, also called Fatty Bodies; the Benzene compounds, also called Aromatic Bodies; the Naphthalene compounds; and the Anthracene compounds. The first two groups comprise by far the largest number of carbon compounds.

METHANE DERIVATIVES. (FATTY BODIES.)

First Group.

Bodies derived from the Hydrocarbons C_nH_{2n+2}.

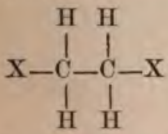
The constitution of methane has been considered above (see *ante*, p. 125). It was also shown that by the linking of carbon atoms to each other the possibility is given for the formation of an homologous series, the members of which differ from each other by CH_2, or a multiple of this. The following members of this series have been particularly well studied.

Methane,	CH_4.	Pentane,	C_5H_{12}.
Ethane,	C_2H_6.	Hexane,	C_6H_{14}.
Propane,	C_3H_8.	Heptane,	C_7H_{16}.
Butane,	C_4H_{10}.		

In speaking of substitution products it was stated that only one mono-substitution product of methane could exist, according to the views now held concerning constitution. The same thing is true of other substitution products in which more than one substituting group is present. Further, we can only conceive of one variety of methane itself, and only one variety has ever been observed.

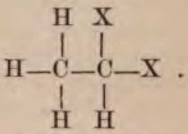
Derivatives of Ethane, C_2H_6.—Only one variety of this hydrocarbon can exist, and only one variety has been observed. Of its mono-substitution products also, only one variety can exist, and only one variety has been observed.

Of the bi-substitution products, however, two varieties are possible, as may be seen by comparing the following formulas:—



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ X & — & C & — & C & — & X \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

and

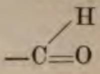
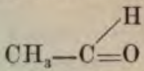


$$\begin{array}{ccccccc} & & H & & X & & \\ & & | & & | & & \\ H & — & C & — & C & — & X \\ & & | & & | & & \\ & & H & & H & & \end{array} .$$

In the first, the substituting groups are in combination with different carbon atoms; in the second, both substituting groups are in combination with the same carbon atom.

A number of compounds are known belonging to the classes of which these are the general formulas. X may represent any of the substituting groups with which we have had to deal; or the class groups CH_2OH, COH, $COOH$, etc.

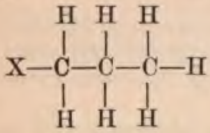
The simplest of these are the chlorides, one of which is $CHCl_2.CH_3$, and the other $CH_2Cl.CH_2Cl$. The first is called ethylidene chloride, the second, ethylene chloride. The constitution of these compounds follows from the following facts:—

Ethylidene chloride is produced by the action of phosphorus pentachloride on aldehyde. We have seen that an aldehyde contains the group  $—\overset{H}{C}{=}O$. Ordinary aldehyde is  $CH_3—\overset{H}{C}{=}O$. As, in the reaction with phosphorus chloride, the oxygen is simply replaced by chlorine, the constitution $CH_3—CHCl_2$ follows for ethylidene chloride. As a consequence, the formula— $CH_2Cl.CH_2Cl$ must be that of ethylene chloride.

Other compounds closely related to these two chlorides will be considered under the heads of ethylene, bibasic acids, etc.

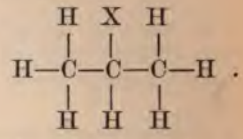
Derivatives of Propane, C_3H_8.—Propane may be considered as a mono-substitution product of ethane, derived from the latter by replacing an atom of hydrogen with CH_3. From what was said above, it will, hence, be seen that only one variety of propane can exist; only one variety has been observed.

Under the head of substitution products, it has been shown that there are two kinds of carbon atoms and, consequently, two kinds of hydrogen atoms in propane (which see); and hence, further, that two different mono-substitution products may be obtained from this hydrocarbon. These have the general formulas:—



$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ X— & C & — & C & — & C & —H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

and



$$\begin{array}{ccccccc} & H & & X & & H & \\ & | & & | & & | & \\ H— & C & — & C & — & C & —H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}.$$

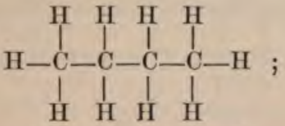
The compounds represented by the first formula are known as propyl compounds; those represented by the second formula as isopropyl or pseudopropyl compounds.

The two alcohols, normal propyl alcohol—$CH_3.CH\,.CH_2OH$, and pseudopropyl alcohol—$CH_3.CHOH.CH_3$, are the starting-points for the preparation of the two series of isomeric propyl compounds. As the former is a primary alcohol, it follows, from what has been said concerning these alcohols, that it must contain the group CH_2OH. This it can only do if the hydroxyl group is in combination with one of the terminal carbon atoms. Consequently, the above constitution is assigned to it. By replacing the hydroxyl by chlorine, bromine, iodine, cyanogen, etc., corresponding derivatives are obtained.

Pseudopropyl alcohol is obtained from acetone and, being a secondary alcohol, contains the group $CH.OH$. Consequently, its hydroxyl is in combination with the central carbon atom of propane. By replacing the hydroxyl with chlorine, bromine, iodine, cyanogen, etc., corresponding pseudopropyl derivatives are obtained.

Derivatives of Butane, C_4H_{10}.—Butane may be considered as a mono-substitution product of propane, consequently, two varieties must be possible, one of which would have the formula—

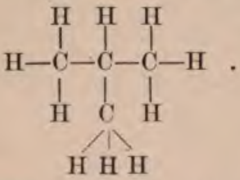
I.



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array} ;$$

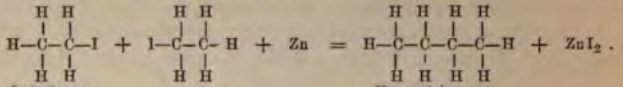
while the other would have the formula—

II.



As a matter of fact, two varieties of butane are known to us, viz., normal butane and trimethylmethane. The former has the constitution represented by formula I. above; the latter that represented by formula II.

Proofs.—The proof of the formula of normal butane is the same in nature as that given for ethane (see p. 127). It is formed by the action of zinc or sodium on ethyl iodide, according to the equation:—

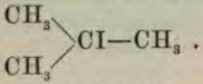


$$\begin{array}{c}H\ H\\ |\ \ |\\ H-C-C-I\\ |\ \ |\\ H\ H\end{array} + \begin{array}{c}H\ H\\ |\ \ |\\ I-C-C-H\\ |\ \ |\\ H\ H\end{array} + Zn = \begin{array}{c}H\ \ H\ \ H\ \ H\\ |\ \ \ |\ \ \ |\ \ \ |\\ H-C-C-C-C-H\\ |\ \ \ |\ \ \ |\ \ \ |\\ H\ \ H\ \ H\ \ H\end{array} + ZnI_2 .$$

Iodethane. Normal butane.

Of course, we here assume that we know the formula of iodethane, but we have already presented good grounds for this assumption. Starting with this formula, we are led very easily to the above formula of normal butane.

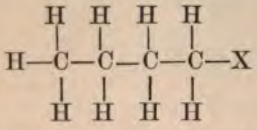
Trimethylmethane is obtained from pseudobutyl iodide, the constitution of which is known to be—



When the iodine is replaced by hydrogen, the hydrocarbon is the product. (See Pseudobutyl Alcohol.)

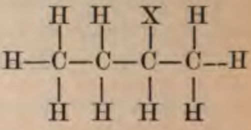
Of normal butane, two kinds of simple substitution products are possible, of the general formulas:—

I.



$$\begin{array}{c}H\ \ H\ \ H\ \ H\\ |\ \ \ |\ \ \ |\ \ \ |\\ H-C-C-C-C-X\\ |\ \ \ |\ \ \ |\ \ \ |\\ H\ \ H\ \ H\ \ H\end{array}$$

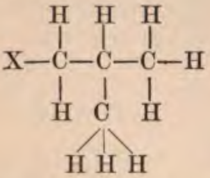
and II.



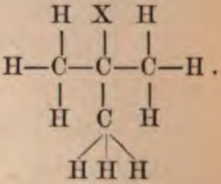
$$\begin{array}{c}H\ \ H\ \ X\ \ H\\ |\ \ \ |\ \ \ |\ \ \ |\\ H-C-C-C-C-H\\ |\ \ \ |\ \ \ |\ \ \ |\\ H\ \ H\ \ H\ \ H\end{array}$$

Of trimethylformene, there are also two kinds possible, of the formulas—

III.



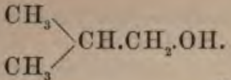
and IV.



Representatives of all four kinds of substitution products are known. The principal of these are the alcohols.

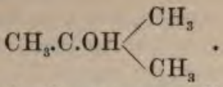
1. Normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2.OH$.
2. Secondary butyl alcohol, $CH_3.CH.OH.CH_2.CH_3$.

3. Isobutyl alcohol,



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CH.CH_2.OH.$$

4. Tertiary butyl alcohol,



$$CH_3.C.OH\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}.$$

From each of these alcohols the corresponding chlorides, bromides, etc., can easily be obtained.

Proofs.—Normal butyl alcohol is obtained indirectly from normal butyric acid, the constitution of which is known.

Secondary butyl alcohol is converted by oxidation into ethyl-methyl-acetone, $C_2H_5—CO—CH_3$. It is, hence, a secondary alcohol, and its constitution is that expressed above.

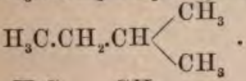
Isobutyl alcohol is converted into isobutyric acid by oxidation. The constitution of the acid is known, and hence also that of the alcohol.

Tertiary butyl alcohol is a tertiary alcohol, and hence contains the group COH. It is prepared by treating acetyl chloride, $CH_3.COCl$, with zinc methyl, $Zn(CH_3)_2$, and hence contains three groups CH_3. The only formula which is in accordance with these facts is that above assigned to the alcohol.

Derivatives of Pentane, *C_5H_{12}*.—Three varieties of pentane may exist. These have the formulas:—

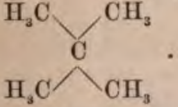
1. $H_3C.CH_2.CH_2.CH_2.CH_3$.

2.



$$H_3C.CH_2.CH\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}.$$

3.



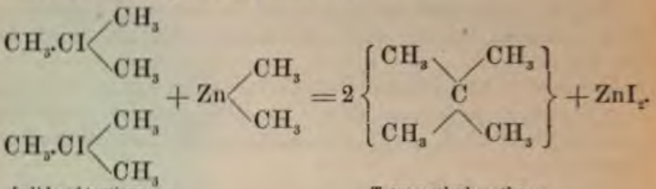
All three of these compounds are known. The first is *normal pentane;* the second is *ethyldimethyl methane;* and the third *tetramethyl methane.*

Proofs.—Normal pentane is obtained by replacing the CN group of the cyanide of normal butane by hydrogen.

We have seen above how the formula of the cyanide itself is determined.

Ethyldimethyl methane is derived from ordinary amyl alcohol, and hence has the same general constitution. The proofs for the constitution of this alcohol will be given below.

Tetramethyl methane is derived from the iodide of tertiary butyl alcohol by the action of zinc methyl. The reaction takes place as follows:—

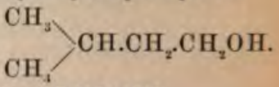


Iodide of tertiary butyl alcohol. Tetramethyl methane.

A great variety of substitution products can be obtained from the isomeric butanes. Of the alcohols five are known, as follows:—

1. Normal amyl alcohol, $CH_3.CH_2.CH_2.CH_2.CH_2OH$.

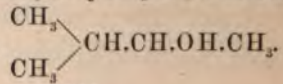
2. Amyl alcohol of fermentation,



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \Big> CH.CH_2.CH_2OH.$$

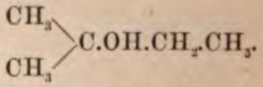
3. Isoamyl alcohol, $CH_3.CH_2.CH_2.CH\,OH.CH_3$.

4. Amylene hydrate,



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \Big> CH.CH.OH.CH_3.$$

5. Tertiary amyl alcohol,



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \Big> C.OH.CH_2.CH_3.$$

These alcohols, like the others which have been considered, form the starting-points for the preparation of corresponding substitution products.

Proofs.—Normal amyl alcohol is obtained from normal valeric acid, and yields this acid by oxidation. The constitution of the acid follows from its method of preparation. (See Normal Valeric Acid.)

Amyl alcohol of fermentation is obtained from ordinary valeric acid by reduction, and is converted into this acid by oxidation. Hence its constitution is similar to that of the acid (which see).

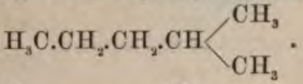
Isoamyl alcohol is a secondary alcohol obtained from methyl propylketone. The constitution of the latter being given, that of the alcohol follows.

Amylene hydrate is a secondary alcohol, the constitution of which is believed to be represented by the above formula. Good proofs are lacking.

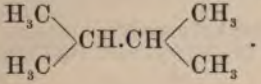
Tertiary amyl alcohol is formed from propionyl chloride and zinc methyl, and, being tertiary, must contain the group COH. The only formula which is in harmony with these facts is that given above.

Derivatives of Hexane, C_6H_{14}.—Three varieties of hexane are known. These are

1. Normal hexane, $H_3C.CH_2.CH_2.CH_2.CH_2.CH_3$.



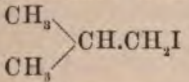
2. Ethyl isobutane, $H_3C.CH_2.CH_2.CH\left<\begin{matrix}CH_3\\CH_3\end{matrix}\right.$.



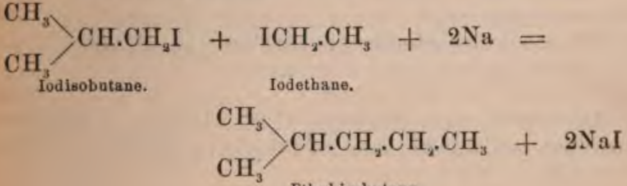
3. Diisopropane, $\left.\begin{matrix}H_3C\\H_3C\end{matrix}\right>CH.CH\left<\begin{matrix}CH_3\\CH_3\end{matrix}\right.$.

Proofs.—Proofs for the first formula are wanting.

The constitution of ethyl isobutane follows from its method of preparation, which consists in treating a mixture of iodethane and iodisobutane with sodium.

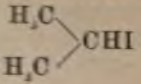


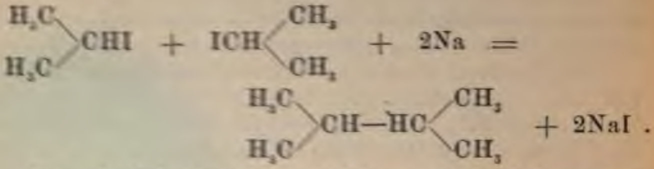
Iodisobutane, being obtained from isobutyl alcohol, has the constitution $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH.CH_2I$. Hence the reaction may be represented thus:—



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH.CH_2I + ICH_2.CH_3 + 2Na = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CH.CH_2.CH_2.CH_3 + 2NaI$$

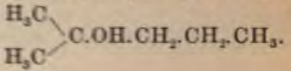
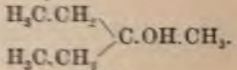
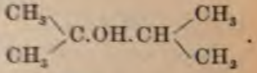
Iodisobutane. Iodethane. Ethyl isobutane.

Diisopropane is obtained by treating iodisopropane with sodium. This iodide, being derived from isopropyl alcohol, has the constitution  $\left.\begin{matrix}H_3C\\H_3C\end{matrix}\right\rangle CHI$. Hence the reaction is



$$\left.\begin{matrix}H_3C\\H_3C\end{matrix}\right\rangle CHI + ICH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. + 2Na =$$
$$\left.\begin{matrix}H_3C\\H_3C\end{matrix}\right\rangle CH-HC\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. + 2NaI .$$

Five alcohols are known which are derived from these varieties of hexane. They are:—

1. Primary hexyl alcohol, $H_3C.CH_2.CH_2.CH_2.CH_2.CH_2OH$.
2. Secondary hexyl alcohol, $H_3C.CH_2.CH_2.CH_2.CH.OH.CH_3$.
3. Dimethyl propyl carbinol,  $\left.\begin{matrix}H_3C\\H_3C\end{matrix}\right\rangle C.OH.CH_2.CH_2.CH_3$.
4. Diethyl methyl carbinol,  $\left.\begin{matrix}H_3C.CH_2\\H_3C.CH_2\end{matrix}\right\rangle C.OH.CH_3$.
5. Dimethyl pseudopropyl carbinol,  $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle C.OH.CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$.

Proofs.—Good proofs for the first formula are wanting. Secondary hexyl alcohol yields by partial oxidation methyl butyl ketone. It is consequently a secondary alcohol, and contains the groups CH_3 and $CH_2.CH_2.CH_2.CH_2$. This gives the above formula.

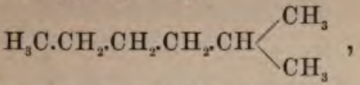
Dimethyl propyl carbinol is obtained from butyryl chloride and zinc methyl.

Diethyl methyl carbinol is obtained from acetyl chloride and zinc ethyl.

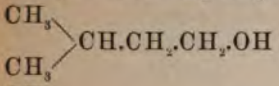
Dimethyl pseudopropyl carbinol is obtained from isobutyryl chloride and zinc methyl.

Derivatives of Heptane, C_7H_{16}.—Three varieties of heptane are known, one of which is probably *normal heptane.*

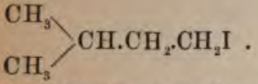
A second variety, *ethyl-amyl*,



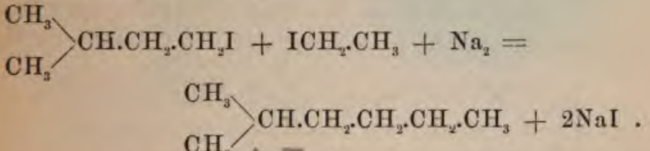
is obtained by the action of sodium on a mixture of ethyl and amyl iodides, the latter from ordinary amyl alcohol. Ordinary amyl alcohol is



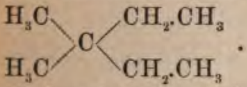
. Consequently the iodide is



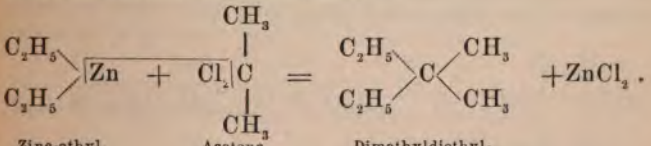
. The reaction is represented by the following equation:—



A third variety of ~~hexane~~ heptane is *dimethyldiethylmethane*,



. This is obtained from zinc-ethyl and acetone chloride, thus:—



Zinc-ethyl. Acetone chloride. Dimethyldiethylmethane.

Acetone chloride, being produced by the replacement of the oxygen of acetone with chlorine, must have the above constitution.

Some of the alcohols corresponding to these hydrocarbons are known. The constitution of these is readily understood so soon as we know the methods of their formation.

Not much is known concerning the constitution of the remaining hydrocarbons of the methane series or their derivatives.

Monobasic, Monatomic Acids, $C_nH_{2n}O_2$.—The acids of this series may be considered as substitution products of the hydrocarbons formed by replacing a hydrogen atom of the latter with carboxyl (COOH). In most cases, these acids have been prepared by converting the group CN of the cyanides of hydrocarbon residues into COOH. If we then know the constitution of the cyanide, the constitution of the acid is readily deduced.

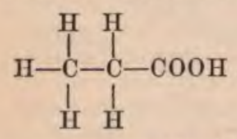
The principal members of the series are

Formic acid,	H.COOH.
Acetic acid,	CH_3.COOH.
Propionic acid,	C_2H_5.COOH.
Butyric acid,	C_3H_7.COOH.
Valeric acid,	C_4H_9.COOH.
Caproic acid,	C_5H_{11}.COOH.

Of formic acid and its substitution products only one variety is known.

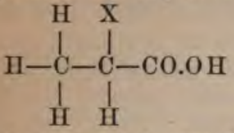
Of acetic acid and its substitution products, also, only one variety is known.

Propionic Acid.—With propionic acid the case is different. Of the acid itself only one variety is known, but of the mono-substitution products two varieties are known. The constitution of the acid is



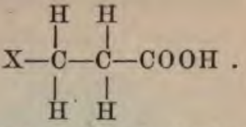
$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-COOH\ .$$

Now it is plain that, in this compound, aside from the hydrogen of the carboxyl group, there are two kinds of hydrogen atoms—those combined with a carbon atom which in its turn is in combination with the group CH_2; and those in combination with a carbon atom which in its turn is in combination with two carbon atoms. The case is similar to that of propane, of which we saw that two varieties of substitution products are possible. Here we have the two possibilities expressed by the formulas



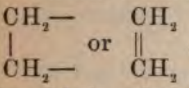
$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{X} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{CO.OH} \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

and



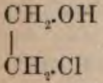
$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{X}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{COOH}\ . \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

Products of the first kind are designated as α-substitution products; those of the second kind as β-substitution products. The best representatives of these two classes of compounds are the two lactic acids (which see). Lactic acids are derived from propionic acid by replacing a hydrogen atom of the latter with hydroxyl. One of the two lactic acids is obtained indirectly from ethylene, which will be shown to have the formula



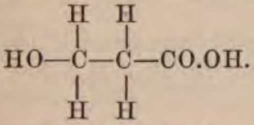
$$\begin{array}{l} \mathrm{CH_2}- \\ | \\ \mathrm{CH_2}- \end{array} \quad \text{or} \quad \begin{array}{l} \mathrm{CH_2} \\ \| \\ \mathrm{CH_2} \end{array}$$

. To this body hypochlorous acid may be added, and the constitution of the resulting compound is



$$\begin{array}{l} \mathrm{CH_2.OH} \\ | \\ \mathrm{CH_2.Cl} \end{array}$$

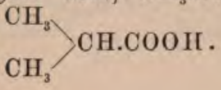
. From this, by treatment with potassium cyanide, KCN, is obtained the corresponding cyanide, which, when boiled with alkalies, yields lactic acid of the constitution



$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{HO}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{CO.OH}. \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

Now, by replacing the hydroxyl group of this acid with chlorine, bromine, etc., β-mono-substitution products are formed. The isomeric compounds of the α-series are those which cannot be prepared in the manner described, and are of the same composition as those obtained from β-lactic acid.

Butyric Acids.—Two acids of the formula $C_3H_7.COOH$ are theoretically possible, and two are known. These are *normal butyric acid*, $CH_3.CH_2.CH_2.COOH$, and *isobutyric acid*,



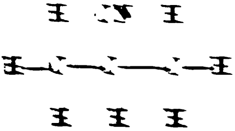
$$\begin{array}{l} \mathrm{CH_3} \\ \mathrm{CH_3} \end{array}\!\!>\mathrm{CH.COOH}\ .$$

Proofs.—Normal butyric acid is prepared by introducing the group C_2H_5 into acetic acid, thus:—

$$CH_2Na.COOH + C_2H_5I = C_2H_5.CH_2.COOH + NaI.$$

Further, by reduction, normal butyric acid yields one of the two possible primary butyl alcohols. It was shown (p. [illegible]) that the other possible primary butyl alcohol is not a derivative of normal butane; consequently normal butyric acid must be derived from normal butane, and it has the formula above assigned to it.

Isobutyric acid is obtained from isopropyl cyanide (p. [illegible]), and this has been shown to have the constitution



$$\begin{array}{ccccccc} & & H & & CN & & H \\ & & | & & | & & | \\ H & — & C & — & C & — & C — H \\ & & | & & | & & | \\ & & H & & H & & H \end{array}$$

From this the above constitution follows for isobutyric acid.

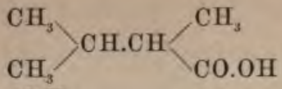
Valeric Acids.—Two are well known, viz. *normal valeric acid*, $CH_3.CH_2.CH_2.CH_2.COOH$, and *ordinary valeric acid*,

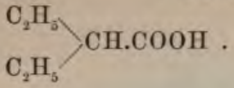
$$\begin{array}{l} CH_3 \\ \quad > CH.CH_2.COOH. \\ CH_3 \end{array}$$

Proofs.—The cyanide from normal butyl alcohol must have the formula $CH_3.CH_2.CH_2.CH_2.CN$. By conversion of the CN group into CO.OH this cyanide yields normal valeric acid.

The cyanide from isobutyl alcohol must have the formula $\begin{array}{l} CH_3 \\ \quad > CH.CH_2.CN. \\ CH_3 \end{array}$ This yields ordinary valeric acid.

Caproic Acids.—Four of these acids are known. They are *normal caproic acid*, $CH_3.CH_2.CH_2.CH_2.CH_2.COOH$; *ordinary caproic acid*, $\begin{array}{l} CH_3 \\ \quad > CH.CH_2.CH_2.COOH; \\ CH_3 \end{array}$

isocaproic acid,  ; and

pseudocaproic acid,  .

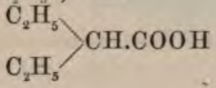
Proofs.—The cyanide from normal amyl alcohol yields normal caproic acid.

Ordinary caproic acid is obtained from the cyanide of ordinary amyl alcohol.

Isocaproic acid is prepared from the cyanide corresponding to amylene hydrate.

Pseudocaproic acid is obtained by introducing two groups, C_2H_5, into acetic acid, thus:—

$CHNa_2.COOH + 2(C_2H_5I) =$

 $+ 2NaI$.

The other acids of this series are not very well known. By the aid of the foregoing examples, the method of determining the constitution of the known acids will be readily understood.

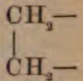
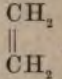
Aldehydes.—Corresponding to every primary alcohol and to every acid there is an aldehyde. The constitution of each of these aldehydes is given if we know from which acid or from which alcohol it is obtained.

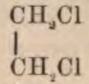
The aldehydes are produced from the primary alcohols by partial oxidation; and from the acids by subjecting a mixture of a salt of the acid and a salt of formic acid to dry distillation.

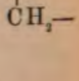
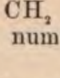
Acetones or Ketones.—The ketones are obtained by distilling mixtures of two acids. If the constitution of the acids is known, that of the ketone obtained in each case is also known.

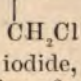
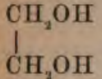
Second Group.

Bodies obtained from the Hydrocarbons C_nH_{2n}.

If carbon is always quadrivalent, then the members of this series of hydrocarbons are either unsaturated, or in them the carbon atoms are united by more than one affinity each. Thus ethylene, C_2H_4, is either  $\begin{array}{l} CH_2- \\ | \\ CH_2- \end{array}$, an unsaturated compound, or it is  $\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}$, in which the two carbon atoms are united by means of two affinities each. Up to the present no proofs have been given for either of these formulas. In regard to these hydrocarbons, we only know that they easily take up two atoms of monovalent elements.

Ethylene and Derivatives.—In connection with ethane derivatives it was stated that two chlorides are known, both of which have the formula $C_2H_4Cl_2$. One of these is obtained from aldehyde by replacing the oxygen atom with two chlorine atoms; hence its formula was assumed to be $CHCl_2.CH_3$. The isomeric compound has the formula  $\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$.

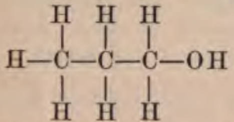
This latter compound is obtained from ethylene by direct addition of chlorine, whence it is concluded that ethylene itself is symmetrical, *i. e.*, that each carbon atom in it holds in combination two hydrogen atoms, giving the constitution expressed by the formula  $\begin{array}{l} CH_2- \\ | \\ CH_2- \end{array}$ or  $\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}$.

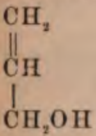
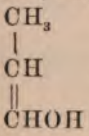
A number of products are known corresponding to ethylene chloride,  $\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$, among which may be mentioned the bromide, iodide, and cyanide. By replacing the chlorine or bromine of ethylene chloride or bromide with hydroxyl, an alcohol is obtained of the constitution  $\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$, which is the simplest representative of the diatomic alcohols or glycols.

Propylene, etc.—The remaining hydrocarbons of this series are obtained for the most part by treating the chlorides, bromides, or iodides of the hydrocarbons of the methane series with alcoholic potassa, by which means ClH, BrH or IH is abstracted from the compound. Thus, from C_3H_7I we obtain C_3H_6; from C_4H_9I we obtain C_4H_8, etc.

In many cases the method of formation of the hydrocarbon leads us directly to its constitution. In some cases a doubt exists even after all the methods of formation and the products of decomposition are taken into consideration.

Alcohols.—Theoretically, a series of alcohols is possible, derived from the hydrocarbons of the ethylene series by the replacement of one hydrogen atom with one hydroxyl group. Only one such alcohol is known. This is allyl alcohol, $C_3H_5.OH$, or $CH_2{=}CH.CH_2.OH$.

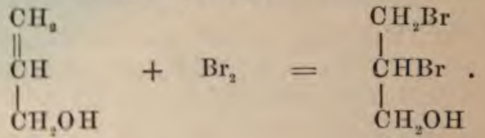
Proofs.—Allyl alcohol differs from propyl alcohol in containing two hydrogen atoms less. Now, by treating allyl alcohol with nascent hydrogen, it is converted into normal propyl alcohol, which, as we have seen, has the constitution  $\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ H & - & C & - & C & - & C-OH \\ & & | & & | & & | \\ & & H & & H & & H \end{array}$. Hence it is assumed that in allyl alcohol, as well as in propyl alcohol, the hydroxyl is in combination with one of the terminal carbon atoms, and, accordingly, it must be either—

 $\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array}$ or  $\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CHOH \end{array}$. If the second formula were

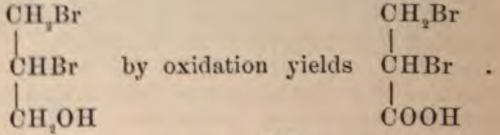
correct we should expect allyl alcohol to yield acetic acid by oxidation, inasmuch as it contains the group CH_3 in combination with another carbon atom. Not a trace of acetic acid is formed, however, and hence the first of the two formulas above given is usually accepted. The proofs for this formula are not positive.

By replacing the hydroxyl of allyl alcohol with chlorine, bromine, iodine, cyanogen, etc., the corresponding chloride, bromide, iodide, and cyanide are obtained.

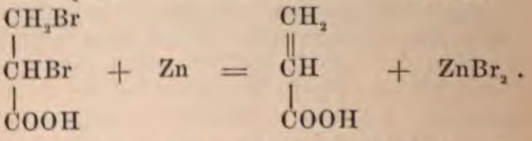
Acids.—Though allyl alcohol is primary, it cannot be directly oxidized to form a corresponding acid. But if the alcohol is first combined with bromine and then oxidized, a bibrompropionic acid is obtained which, when again freed of bromine, yields acrylic acid. These reactions strengthen the conclusion above drawn, viz., that allyl alcohol contains the group CH_2OH. The reactions are—

1.


$$\begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} + Br_2 = \begin{array}{c} CH_2Br \\ | \\ CHBr \\ | \\ CH_2OH \end{array}.$$

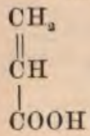
2.


$$\begin{array}{c} CH_2Br \\ | \\ CHBr \\ | \\ CH_2OH \end{array} \text{ by oxidation yields } \begin{array}{c} CH_2Br \\ | \\ CHBr \\ | \\ COOH \end{array}.$$

3.


$$\begin{array}{c} CH_2Br \\ | \\ CHBr \\ | \\ COOH \end{array} + Zn = \begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ COOH \end{array} + ZnBr_2.$$

From these changes we are led to the formula—



$$\begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ COOH \end{array}$$

for acrylic acid. This acid is the first of a series each of which differs from the corresponding member of the series $C_n H_{2n} O_2$ by containing two hydrogen atoms less.

The member succeeding acrylic acid in this series is crotonic acid, to which the constitutional formula—$CH_2{=}CH{-}CH_2{-}CO.OH$ is usually assigned. The grounds for this are as follows:—

Allyl cyanide, as has been shown, has the formula $CH_2{=}CH{-}CH_2.CN$. This cyanide, when properly treated, is converted into crotonic acid.

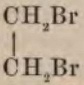
When treated with nascent hydrogen, it yields normal butyric acid, which shows that the carboxyl group of crotonic acid is in combination with one of the terminal carbon atoms.

Similar considerations lead to a knowledge of the constitution of the remaining members of this series. None of these, however, have been investigated as fully as acrylic and crotonic acids.

Third Group.

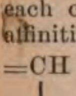
Bodies derived from the Hydrocarbons $C_n\,H_{2n-2}$.

When ethylene bromide,



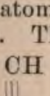
$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}$$

, is heated with alcoholic potassa, two molecules of hydrobromic acid are given off and a compound of the formula C_2H_2 is produced, which is the first of a series of similar hydrocarbons. Just as ethylene must be considered either as unsaturated or as having its carbon atoms combined by the action of more than one affinity of each atom, so also with the hydrocarbon C_2H_2, or acetylene. In the latter case, however, if the compound is unsaturated, each carbon atom must be united by means of three affinities each. The formula of acetylene is, accordingly,



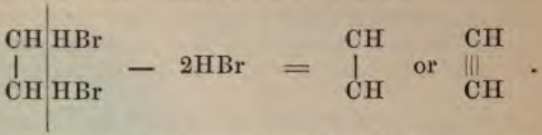
$$\begin{array}{l} =CH \\ \;\;| \\ =CH \end{array}$$

, or



$$\begin{array}{c} CH \\ ||| \\ CH \end{array}$$

. The latter formula is usually accepted, though the grounds for it are weak. However, whether this treble union exists between the carbon atoms or not, we can be moderately certain that acetylene, like ethylene, is symmetrically constructed, *i. e.*, that each carbon atom is in combination with one hydrogen atom. This follows from the fact that acetylene is formed by abstracting hydrobromic acid from ethylene bromide. For the latter compound has the formula $\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}$, and it appears most probable that the splitting off of BrH would take place as follows:—



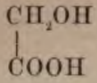
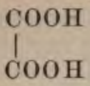
$$\left.\begin{array}{l}CH\\ |\\ CH\end{array}\right|\begin{array}{l}HBr\\ \\ HBr\end{array} \quad - \quad 2HBr \quad = \quad \begin{array}{c}CH\\ |\\ CH\end{array} \quad \text{or} \quad \begin{array}{c}CH\\ |||\\ CH\end{array}.$$

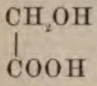
Acetylene and its homologues have this common property, they each combine with four atoms of chlorine or bromine, thus forming saturated compounds, which may be regarded as substitution products of the hydrocarbons of the marsh-gas series. Very little is known regarding the constitution of the higher members of the series. No alcohols are known corresponding to the above hydrocarbons.

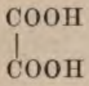
A few acids have been studied, the general formula of which is $C_nH_{2n-4}O_2$, which may be considered as derived from the hydrocarbons of the acetylene series by replacing a hydrogen atom with carboxyl. Their constitution is in no case well known.

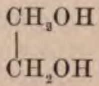
Fourth Group.

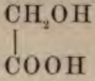
Diatomic Alcohols and Acids.

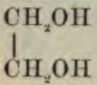
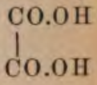
It has been stated that when we replace the bromine of ethylene bromide with hydroxyl, an alcohol of the constitution $\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\end{array}$ is obtained. Alcohols of this kind which contain two hydrogen groups are called *diatomic alcohols* or *glycols*. The best studied diatomic alcohol is the one the constitutional formula of which is given above. This is ethylene alcohol or ethylglycol. If the above formula is correct, we are justified in expecting that ethylene alcohol will yield two products by oxidation. The first would be formed if only one of the groups CH_2OH were converted into COOH. It would have the constitution  $\begin{array}{l}CH_2OH\\ |\\ COOH\end{array}$. The second would be formed if both the groups CH_2OH were converted into COOH. It would be  $\begin{array}{l}COOH\\ |\\ COOH\end{array}$. Both these products are actually known, and may be obtained by the oxidation of ethylene alcohol. They are both representatives of new classes of compounds, the nature of which may be easily understood.

The compound  $\begin{array}{l}CH_2OH\\ |\\ COOH\end{array}$, or glycolic acid, is half alcohol and half acid, and it can be shown to possess the properties of both. It is acetic acid in which one hydrogen atom has been replaced by hydroxyl, or oxyacetic acid. The acids of which it is the representative are known as *oxyacids.*

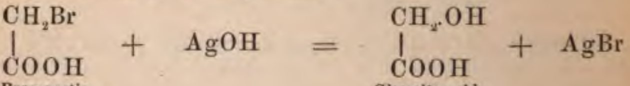
The compound  $\begin{array}{l}COOH\\ |\\ COOH\end{array}$ is an acid, and, from what was said concerning acids in general, it will be recognized as a bibasic acid. It is known as oxalic acid. It is the first of a series of *bibasic acids.*

Diatomic Alcohols, $C_nH_{2n+2}O_2$.—Ethylene alcohol is the only member of this series that is well known. In regard to its constitution enough has been said above to show upon what grounds the formula  $\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$ rests. We may obtain a great variety of derivatives from this alcohol by replacing one or both of its hydroxyl groups with monovalent elements or groups. The products obtained by the addition of various elements or groups to ethylene may also be considered as derivatives of ethylene alcohol.

Diatomic Acids, $C_nH_{2n}O_3$.—The acids of which glycolic acid,  $\begin{array}{l}CH_2OH\\ |\\ COOH\end{array}$, is the simplest known are, as has been said above, half alcohols and half acids, the alcoholic character being imparted to them by the presence of the group OH, in combination with unoxidized carbon, and the acid character by the presence of the group COOH. All that has been said in regard to the alcoholic group OH holds good in regard to that group in these diatomic acids; and all that has been said in regard to the carboxyl group holds good in regard to that group in these acids.

That the above formula for glycolic acid is correct, follows from the methods of its preparation. It is a product of the partial oxidation of ethylene alcohol—  $\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$, one of the primary alcohol groups being converted into carboxyl. The fact that glycolic acid itself by further oxidation is converted into oxalic acid,  $\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array}$ proves also that the group CH_2OH is present in it.

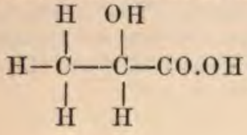
It is further obtained by treating chlor- or bromacetic acid with silver oxide, thus:—



$$\begin{array}{l}CH_2Br\\ |\\ COOH\end{array} + AgOH = \begin{array}{l}CH_2.OH\\ |\\ COOH\end{array} + AgBr.$$

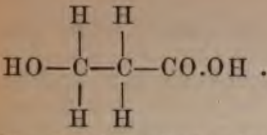
Bromacetic acid. Glycolic acid.

Lactic or *oxypropionic acid* is the succeeding homologue of glycolic or oxyacetic acid. As it is a monosubstitution product of propionic acid, there must be two varieties possible corresponding to α- and β-chlorpropionic acids. One of these would have the formula—



$$\begin{array}{ccccc} & H & & OH & \\ & | & & | & \\ H- & C & - & C & -CO.OH\\ & | & & | & \\ & H & & H & \end{array},$$

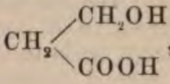
and the other, the formula—

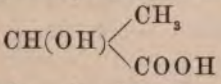


$$HO-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-CO.OH$$

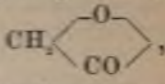
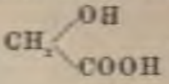
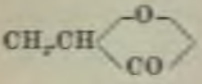
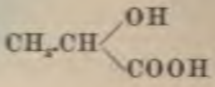
. Both of these acids are known.

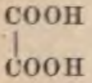
The first is *ordinary lactic acid*, or *ethylidenelactic acid.* The second is *sarcolactic acid*, or *ethylene lactic acid.*

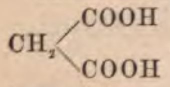
Proofs.—The proofs of these formulas are the following: Sarcolactic is obtained by boiling cyanhydrine with alkalies. Cyanhydrine, $\begin{array}{l}CH_2.OH\\ |\\ CH_2.CN\end{array}$, is obtained from ethylene chlorhydrine, $\begin{array}{l}CH_2.OH\\ |\\ CH_2.Cl\end{array}$, by treating the latter with potassium cyanide. Ethylene chlorhydrine is obtained by treating ethylene with hypochlorous acid. Ethylene is $\begin{array}{l}CH_2\\ \|\\ CH_2\end{array}$, as has been shown. Further, sarcolactic acid contains the group CH_2OH, for, by oxidation, it yields an acid containing the same number of carbon atoms. If it contains the group CH_2OH, it must have the constitution represented by the formula , which is that above given.

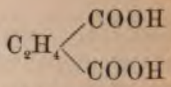
The only other possible compound of this composition must have the formula . Consequently, the latter is the formula of ordinary lactic acid. Such a compound could not, by oxidation, yield an acid containing the same number of carbon atoms. Ordinary lactic acid breaks up by oxidation, yielding both formic and acetic acids.

The remaining diatomic acids of the series have not been as well studied as the few which have here been considered.

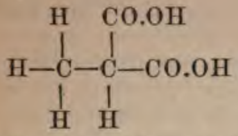
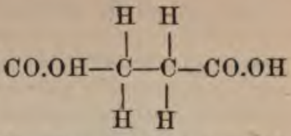
One peculiarity of the above acids should be noticed. They are monobasic acids, but still they are capable of forming anhydrides by losing one molecule of water from one of their own molecules. The anhydrides thus formed differ somewhat from the ordinary anhydrides of acids. Thus we have glycolic anhydride, , formed by abstracting one molecule of water from one molecule of glycolic acid,  $CH_2\langle^{OH}_{COOH}$; lactic anhydride, , formed from one molecule of ordinary lactic acid,  $CH_3.CH\langle^{OH}_{COOH}$.

Bibasic Acids, $C_nH_{2n-2}O_4$.—*Oxalic acid*, $C_2H_2O_4$, or  $\begin{array}{l}COOH\\ |\\ COOH\end{array}$, is the simplest representative of these acids possible. The fact that it is bibasic, and that the number of groups COOH contained in a compound determines its basicity, leads to the formula given.

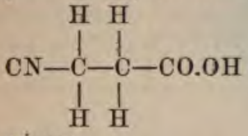
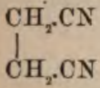
The second member of this series is *malonic acid*,  $CH_2\langle^{COOH}_{COOH}$. Of each of these acids only one variety is possible.

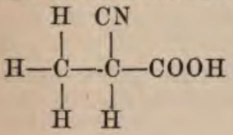
The third member is *succinic acid*,  $C_2H_4\langle^{COOH}_{COOH}$.

Of this there must be two varieties corresponding to the two lactic acids, or the two series of mono-substitution products of propionic acid. For succinic acid may plainly be considered as propionic acid in which a hydrogen atom has been replaced by a carboxyl group. The two succinic acids would have the following formulas:—

1.  $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{CO.OH}{\underset{H}{C}}-CO.OH}$ and 2.  $\mathrm{CO.OH-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CO.OH}$

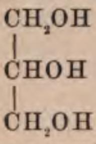
The second formula is that of ordinary *succinic acid*, and the first that of *isosuccinic acid.*

Proofs.—Ordinary succinic acid is obtained from β-cyanpropionic acid, the constitution of which we know to be  $\mathrm{CN-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CO.OH}$; and from ethylene cyanide,  $\begin{array}{l}\mathrm{CH_2.CN}\\ |\\ \mathrm{CH_2.CN}\end{array}$, which is obtained by treating ethylene bromide with potassium cyanide.

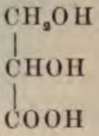
Isosuccinic acid is obtained from α-cyanpropionic acid, which is  $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{CN}{\underset{H}{C}}-COOH}$.

Fifth Group.

Triatomic Alcohols and Acids.

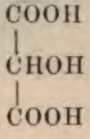
Glycerin.—Only one alcohol is well known which contains three hydroxyl groups. This is glycerin. Such alcohols are known as triatomic alcohols. The formula of glycerin is  $\begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{CH_2OH}\end{array}$. This formula is very probable, because, as a result of a large number of observations of carbon compounds, it seems to be a general fact that one carbon atom cannot hold in combination more than one hydroxyl group. If this is true, the above formula is the only one possible for glycerin. But, again, by oxidation, glycerin yields a monobasic acid containing the same number of carbon atoms; and, by further oxidation, apparently a bibasic acid also containing the same number of carbon atoms. These facts would show that the group CH_2OH occurs twice in glycerin. But if there are two groups CH_2OH present in glycerin, then the formula above accepted must be correct.

Glyceric Acid is obtained by partially oxidizing glycerin. As the acid contains the same number of carbon atoms as glycerin contains, it is assumed that the oxidation consists in a transformation of the primary alcohol group CH_2OH into $COOH$; hence, the formula of glyceric acid is



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

. According to this, a bibasic acid ,



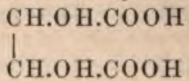
$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

, ought to be obtained by oxidizing glyceric acid, just as this bibasic acid is obtained by oxidizing glycerin. This transformation has not yet been effected.

Sixth Group.

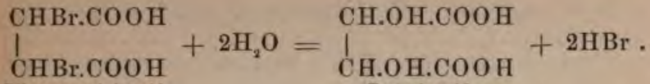
Tetratomic Compounds.

The best known members of this group are *tartaric acid* and *citric acid.* The former is a bibasic acid, containing, in addition to the two carboxyl groups, two alcoholic hydroxyl groups. It is hence a bibasic tetratomic acid. It is dioxysuccinic acid, and must have the formula



$$\begin{array}{l} CH.OH.COOH \\ | \\ CH.OH.COOH \end{array}$$

. It is obtained from dibromsuccinic acid by treating the latter with water, thus:—



$$\begin{matrix} CHBr.COOH \\ | \\ CHBr.COOH \end{matrix} + 2H_2O = \begin{matrix} CH.OH.COOH \\ | \\ CH.OH.COOH \end{matrix} + 2HBr .$$

Dibromsuccinic acid. Tartaric acid

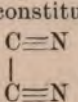
Citric acid is tribasic, containing, in addition to its three carboxyl groups, one alcoholic hydroxyl. It is hence a tribasic tetratomic acid.

In addition to the groups above referred to, there are *pentatomic* and *hexatomic compounds.* Of the former, there is only one representative known. Of the latter, however, a large number of members are known. Among these are the different varieties of sugars, cellulose, and starch; and the acids which are derived from them. All that is positively known of these compounds is that they contain a certain number of hydroxyl groups, or of hydroxyl and carboxyl groups. The presence of the carboxyl groups is detected through the acid properties of the substance. If the substance is a monobasic acid, one carboxyl group is assumed as being present in it; if it is a bibasic acid, two carboxyl groups are assumed as being present in it, etc. The number of hydroxyl groups present is determined by allowing acetyl chloride or acetic anhydride to act upon the compound. If the latter contains only one hydroxyl, it will take up only one acetyl group, C_2H_3O; if it contains two hydroxyl groups, it will take up two acetyl groups, etc.

Seventh Group.

Cyanogen Compounds.

In speaking of the group CN as a substituting group, the proofs for the formula $—C\equiv N$ for this group were given (*ante*, p. 152). Now this same group is obtained from the compounds known as cyanides, and hence the cyanides have an analogous constitution. Cyanogen itself has the formula C_2N_2 or



$\begin{matrix} C\equiv N \\ | \\ C\equiv N \end{matrix}$. The simplest compound of cyanogen is hydrocyanic acid, which consists of the group $—C\equiv N$ combined with hydrogen, viz., $H—C\equiv N$.

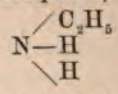
The hydrogen atom of this acid may be replaced by a variety of groups or other elements, as, for instance, OH, SH, NH_2, etc. Then a large number of derivatives are obtained which have a constitution similar to that of the acid. Thus we have *cyanic acid*, $HO—C\equiv N$; *sulphocyanic acid*, $HS—C\equiv N$; *cyanamide*, $H_2N—C\equiv N$, etc.

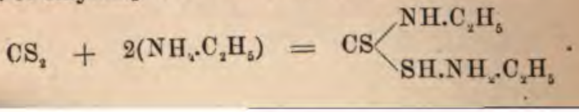
It has already been shown that there are compounds containing the group $C\equiv N—$ called carbylamines, which are isomeric with the cyanides of hydrocarbon residues, and the proofs for the formula $C\equiv N—$ have also been given (see *ante*, p. 153).

Mustard Oils.—Sulphocyanic acid, $HS—C\equiv N$, like other acids, yields salts and ethers by exchanging its hydrogen for metals or hydrocarbon residues. We have potassium sulphocyanate, $KS—C\equiv N$; methyl sulphocyanate, $CH_3—S—C\equiv N$, etc. Running parallel to the ethers of sulphocyanic acid is a series of compounds known as mustard oils. These have the same composition as the above ethers, but entirely different properties and constitution.

The simplest representative of this series is *methyl mustard oil*, which has the constitution expressed by the formula $S=C=N—CH_3$. A number of corresponding compounds are known, one of which is *allyl mustard oil*, $S=C=N—C_3H_5$. This is the oil obtained from black mustard seed.

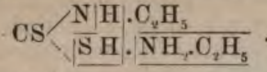
The proofs of the constitution assigned to the mustard oils are as follows:—

Ethyl mustard oil is formed by a somewhat circuitous method. When carbon bisulphide, CS_2, is brought in contact with ethylamine,  $N\begin{cases}C_2H_5\\H\\H\end{cases}$, the ethylamine salt of ethylsulphocarbamic acid is formed, thus:—



$$CS_2 + 2(NH_2.C_2H_5) = CS\begin{cases}NH.C_2H_5\\SH.NH_2.C_2H_5\end{cases}.$$

By appropriate reactions, this salt is split up into ethylamine, hydrogen sulphide, and ethyl mustard oil. The decomposition can be best interpreted as follows:—



$$CS\begin{cases} N\,|H|.C_2H_5 \\ |SH|.|NH_2.C_2H_5| \end{cases}.$$

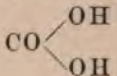
Hence the resulting mustard oil retains an atom of sulphur, combined by means of two affinities with carbon, and the residue of ethylamine, $=N.C_2H_5$, being bivalent, would naturally be held by the two remaining affinities of the carbon. But, if we examine the products of decomposition of ethyl mustard oil, we are also led to the formula above given. With water or hydrochloric acid it yields ethylamine, carbon dioxide, and hydrogen sulphide; with nascent hydrogen it yields ethylamine formylsulphaldehyde and hydrogen sulphide. The production of ethylamine indicates clearly that, in the mustard oil, the ethyl group is in combination with the nitrogen atom; and the production of formylsulphaldehyde, which differs from formic aldehyde, H.COH, only in containing sulphur in the place of oxygen, also indicates that in ethyl mustard oil the sulphur atom is in combination with carbon. These results are embodied in the formula accepted for the mustard oil.

The ether of sulphocyanic acid, which is isomeric with ethyl mustard oil, conducts itself towards reagents in an entirely different manner. It never yields ethylamine, but always yields a compound in which the ethyl group is in combination with sulphur, as ethylsulphide or ethylsulphurous acid; while the nitrogen is split off in combination with hydrogen alone, or with carbon, hydrogen, and oxygen.

Eighth Group.

Derivatives of Carbonic Acid.

The salts of carbonic acid have the general formula M_2CO_3. They are derived from a bibasic acid, H_2CO_3. This acid being bibasic contains two hydroxyl groups, and hence we are led to the formula

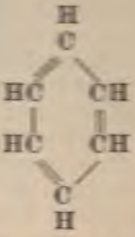


$$CO\begin{cases} OH \\ OH \end{cases}$$

for

from benzene by the introduction of a variety of groups or elements in the place of hydrogen. All these compounds bear a similar relation to benzene to that which the fatty bodies bear to marsh-gas. In studying the aromatic bodies, then, it is plainly our first duty to determine the constitution of benzene itself, as the constitution of the derivatives cannot be understood until this determination is made.

Constitution of Benzene.—The great stability of benzene indicates that it is a saturated compound. Now, if the carbon atoms contained in it are quadrivalent, the simplest hypothesis which can be formed concerning its constitution would be indicated in the following formula:—



According to this, the molecule of benzene consists of a closed chain of carbon atoms, each united, on the one hand, by two affinities with another carbon atom; on the other hand, by one affinity with a second carbon atom.

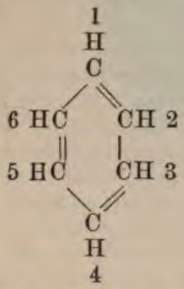
This formula, which was originally proposed by Kekulé, accounts satisfactorily for nearly all the facts known concerning aromatic bodies. These facts are mainly the following:—

1. Of the substitution products of benzene which contain one substituting group, only one variety is known.
2. Of the substitution products of benzene which contain two substituting groups, three varieties have been observed, and only three.
3. Of the substitution products of benzene which contain three substituting groups, more than three varieties have been observed.

If all the hydrogen atoms in benzene play exactly the same parts, then the first fact mentioned would follow as a matter of course. In the above formula, all the hydrogen atoms are represented as playing the same parts. Each one is situated exactly like all the others with reference to the whole molecule.

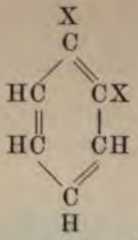
A great many efforts have been made to obtain isomeric mono-substitution products of benzene, but they have all been unsuccessful.

Again, if we examine the above formula carefully, we find that there are three and only three pairs of hydrogen atoms in it which differ from each other in the positions of their individual atoms. Numbering these hydrogen atoms as follows:—



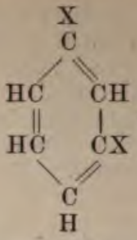
we can distinguish the following pairs: 1.2, 1.3, 1.4, 1.5, 1.6; or, beginning with 2, we would also have five pairs; but, as all the hydrogen atoms of benzene play exactly the same parts, it is plainly immaterial with which one we begin, the resulting pairs will be identical. Thus, 1.2 is identical with 2.3, 3.4, 4.5, and 5.6; 1.3 is identical with 2.4, 3.5, 4.6, and 5.1; 1.4 is identical with 2.5, 3.6, 4.1, and 5.2; etc. But, further, 1.2 is also identical with 1.6, and 1.3 with 1.5. Hence, of the five original pairs we have only three left. These are 1.2, 1.3, and 1.4. They are the only ones that differ from each other essentially in the benzene formula of Kekulé. If, then, substitution products, containing two substituting groups, are obtained from benzene, they have one of the three following formulas, in which X represents a monovalent substituting group or element:—

1.



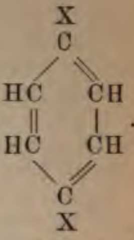
;

2.



;

3.



.

As was stated above, only three varieties of bisubstitution products of benzene have ever been observed. So that here, again, we have perfect harmony between facts and the hypothesis.

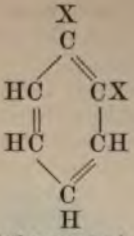
No one claims that the benzene formula of Kekulé represents the actual arrangement of the atoms in space. It undoubtedly represents certain truths, however. It represents that in the molecule of benzene, the hydrogen atoms are arranged symmetrically, and that all the parts of the molecule are symmetrically arranged. We do not know positively that there is such symmetry in the benzene molecule, for we know nothing of molecules themselves, but, from all the facts known to us, it seems fair to conclude that this symmetry of the different parts is characteristic of the benzene molecule.

Substitution Products of Benzene.—Of mono-substitution products we have only one variety. We have only one monochlorbenzene, C_6H_5Cl; only one oxybenzene, or phenole, $C_6H_5.OH$; only one benzoic acid, $C_6H_5.COOH$; only one toluene, $C_6H_5.CH_3$, etc. etc. The constitution of most of these derivatives is very simple. There is a peculiarity, however, connected with those which are formed by replacing one hydrogen atom of benzene with a hydrocarbon residue. The simplest compound formed in this way is toluene, which consists of benzene in which a hydrogen atom has been replaced by the methane residue CH_3; if, instead of the residue CH_3, we introduce C_2H_5, we obtain ethylbenzene, $C_6H_5.C_2H_5$, which is plainly an homologue of toluene; so, also, the residues C_3H_7, C_4H_9, C_5H_{11}, etc., may be employed, and thus we obtain an homologous series of aromatic hydrocarbons, all of which are mono-substitution products of benzene. These may, further, all be regarded as substitution products of the hydrocarbons of the methane series. Accordingly, of toluene and ethylbenzene, which are mono-substitution products of methane and ethane respectively, only one variety each is possible; while of the next homologue, or propylbenzene, $C_6H_5.C_3H_7$, two varieties are possible, corresponding to the α- and β-monosubstitution products of propyl, or to the propyl and isopropyl compounds (which see). The main members of the series of hydrocarbons thus referred to are:—

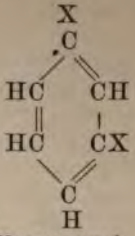
Benzene,	C_6H_6.
Toluene or methylbenzene,	C_7H_8 or $C_6H_5.CH_3$.
Ethylbenzene,	C_8H_{10} or $C_6H_5.C_2H_5$.
Propylbenzene,	C_9H_{12} or $C_6H_5.C_3H_7$.
Butylbenzene,	$C_{10}H_{14}$ or $C_6H_5.C_4H_9$.
Amylbenzene,	$C_{11}H_{16}$ or $C_6H_5.C_5H_{11}$.

Of these hydrocarbons, two kinds of mono-substitution products are possible, viz., those in which the substituting group or element is situated in the *benzene nucleus*, and those in which the substituting group or element is situated in the other residue. These other residues, however they may be constituted, are known as *lateral chains*. It is plain that substitution products of the latter kind correspond closely to those of the hydrocarbons of the methane series, and hence they need no special consideration here. If a substituting group or element enter into the benzene nucleus of any of these hydrocarbons, of course we have no longer to deal with mono-substitution products of benzene.

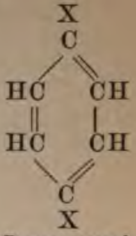
Bisubstitution Products.—The three classes of biderivatives of benzene which we have above recognized as possible, have been designated respectively as *ortho*, *meta*, and *para compounds*, or, by others, as 1.2. 1.3, and 1.4 compounds. The former expressions are to be preferred, for they are independent of any hypothesis concerning the positions of the substituting groups. It is usual to consider the expressions ortho and 1.2, meta and 1.3, para and 1.4, as identical, but this implies that the following formulas have been proved, while they have not been:—



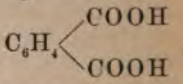
Ortho-compound.



Meta-compound.



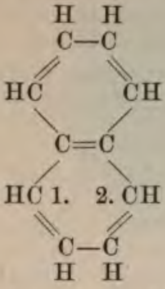
Para-compound.

What we really know is that there are three classes of these bi-substitution products, and that the members of any one of these classes can be converted into each other, thus showing that they are allied. There are three compounds, each representing one of the three classes to which all other bi-substitution products are referred, if possible. If the constitution of any such product is unknown, it is only necessary to convert it into one of the three compounds, when the series to which it belongs is assumed to be known. The three compounds are the isomeric, bicarbonic acids of benzene,  $C_6H_4\begin{cases}COOH\\COOH\end{cases}$, viz., phthalic, isophthalic, and terephthalic acids. All bi-substitution products which can be converted into phthalic acid are known as ortho-compounds; all that can be converted into isophthalic acid are known as meta-compounds; and all that can be converted into terephthalic acid are known as para-compounds.

The conversion into these acids need not always be direct. If it be possible to convert a compound into another which, in its turn, can be converted into one of the above acids, the same conclusion is drawn as in the case of a direct conversion. Of course, the accuracy of the conclusions drawn with reference to the constitution of bi-substitution products depends upon the trustworthiness of the reactions employed in effecting the conversions. Some reactions employed for this purpose have been found to give inaccurate results; that is to say, the products resulting from an application of these reactions belong to different series from those to which the original compounds belonged. It is very probable that some compounds now classified with one series in consequence of some conversion, may be found, by future investigations, to belong to a different series.

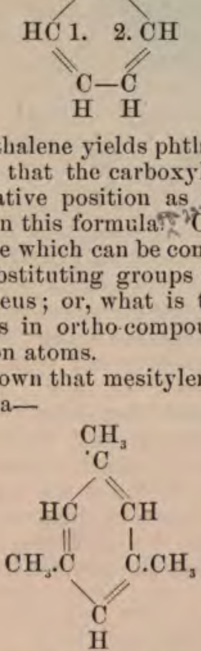
The formulas given above as representing the relative positions of the substituting groups in ortho-, meta-, and para-compounds are based upon the following facts:—

It will be shown that naphthalene (which see) probably has the formula—

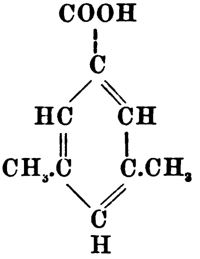


By oxidation, naphthalene yields phthalic acid. It seems probable, therefore, that the carboxyl groups in the acid have the same relative position as that of the groups numbered 1 and 2 in this formula. Consequently, ortho-compounds, or those which can be converted into phthalic acid, have their substituting groups in the positions 1.2 in the benzene nucleus; or, what is the same thing, the substituting groups in ortho-compounds are combined with adjacent carbon atoms.

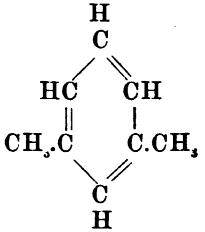
It will also be shown that mesitylene (which see) probably has the formula—



By partially oxidizing this hydrocarbon, an acid is obtained of the formula—



When this acid is heated under proper conditions carbon dioxide is given off and a hydrocarbon is obtained of the formula—



Lastly, when this hydrocarbon is oxidized, both the groups CH_3 are converted into COOH, and the resulting acid is isophthalic. Hence, if the formula of mesitylene is correct, that of isophthalic acid is also correct.

By exclusion, terephthalic acid becomes a 1.4 compound, and, consequently, all para-compounds are 1.4 compounds.

It must be confessed that these proofs are not strong enough to command universal respect among chemists. As the expressions 1.2, 1.3, and 1.4 are in common usage, it is well, however, to know the grounds upon which their use is based. Some of the principal bi-substitution products of benzene are given in the following table, which shows also to which series the compounds belong:—

Ortho.	Meta.	Para.
Phthalic acid.	Isophthalic acid.	Terephthalic acid.
Orthoxylene.	Isoxylene.	Xylene.
Salicylic acid.	Oxybenzoic acid.	Paroxybenzoic acid.
Pyrocatechin.	Resorcin.	Hydroquinone.
Orthodinitrobenzene.	Metadinitrobenzene.	Paradinitrobenzene.
dibrombenzene	Metadibrombenzene.	Paradibrombenzene.

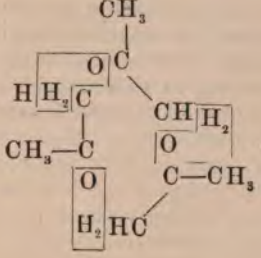
It is well to note here that whether both substituting groups be the same or not, only three kinds of products can be obtained.

Tri-substitution Products.—The most important of the tri-substitution products of benzene is mesitylene. The formula of this hydrocarbon is C_9H_{12}. By oxidation it yields, according to the energy of the reaction, three different products. The first, mesitylenic acid—$C_8H_9.COOH$, is monobasic; the second, uvitic acid—$C_7H_6.(COOH)_2$, is bibasic; and the third, trimesinic acid, $C_6H_3.(COOH)_3$, is tribasic. All of these acids, when heated with lime, yield either benzene itself or derivatives of benzene. Hence, it is concluded that mesitylene is benzene in which three hydrogen atoms are replaced by the residue CH_3 thus, $C_6H_3(CH_3)_3$. By oxidation each one of these groups in turn is converted into carboxyl, yielding thus the three acids above mentioned. It still remains, however, to decide what the positions of these three substituting groups in the benzene nucleus are.

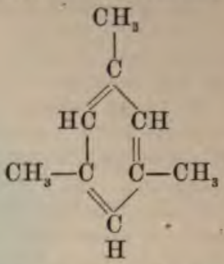
The following method of consideration leads to the formula for mesitylene given on page 217:—

When acetone is treated with concentrated sulphuric acid, water is abstracted and the residues of three molecules unite to form mesitylene. It seems to be fair to assume that the three residues are constituted exactly the same, as they are formed under exactly the same conditions, from the same compound. If they are the same, they must each be C_3H_4. Three such residues might be formed from acetone, thus:—

Acetone is $CH_3—CO—CH_3$; three molecules may be arranged—



If water is abstracted in the manner indicated by the lines, we have left three residues, C_3H_4, and, if these unite, they would form a compound of the constitution represented by the following formula:—



This is the formula accepted for mesitylene; and from this we conclude, as above seen, that meta-compounds have their substituting groups in the positions 1.3.

If this formula is carefully examined, it will be seen that each one of the three hydrogen atoms remaining in the benzene-nucleus occupies a similar position to that occupied by the other two. Accordingly, if this formula is correct, we should expect to find that, by the introduction of one substituting group into mesitylene, only one product would be formed. This has actually been found to be true.

Besides mesitylene, there are many tri-substitution products of benzene known, containing such elements as Cl, Br, I, and such groups as NO_2, NH_2, SO_2OH, etc. The principle, according to which the position of the substituting groups in these compounds is determined, is this: One of the groups is split off, and the constitution of the resulting bi-substitution product is determined as above; then from the original compound some other group is split off, and the constitution of the bi-substitution product resulting in this case also determined. We are thus able to judge of the positions of the three groups with reference to each other. There are not many compounds, however, which can be subjected to this kind of examination with satisfactory results, so that the constitution of these tri-derivatives is not really as well known as that of the bi-derivatives.

Those derivatives of benzene which contain four or five substituting elements or groups have not been very fully investigated.

Also only a few hexa-derivatives are known, the most important of which is *mellitic acid*, $C_6(COOH)_6$, or benzene, in which all six hydrogen atoms are replaced by carboxyl groups.

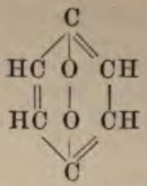
Peculiar Benzene Derivatives. — Among benzene derivatives we find three classes which are not represented among the fatty bodies, and hence they require some attention here. These are the *phenoles*, *quinones*, and *azo-bodies*.

Phenoles.—Phenoles are the oxy-derivatives of benzene and its homologues, formed by the introduction of hydroxyl into the place of hydrogen in the benzene nucleus. The corresponding compounds of the hydrocarbons of the methane series are all alcohols, either primary, secondary, or tertiary. The phenoles are, however, not alcohols in the sense in which that term has been used up to the present. By oxidation they yield neither aldehydes, acids, nor ketones.

The presence of hydroxyl in phenoles can be proved in the same way that it was proved for other bodies containing hydroxyl.

There are monatomic phenoles, containing only one hydroxyl; biatomic phenoles, containing two hydroxyls; triatomic phenoles, containing three hydroxyls, etc.

Quinones.—The quinones are derived from benzene and its homologues by the introduction of two atoms of oxygen in the place of two hydrogen atoms in the benzene-nucleus. Thus the simplest quinone has the formula $C_6H_4O_2$. The two oxygen atoms are supposed to form a bivalent group, —O—O—, by combining with each other by means of one of their affinities each. Most quinones are derived from para-compounds by oxidation, as from hydroquinone, and hence it is concluded that the hydrogen atoms replaced by the bivalent group —O—O— in the formation of quinones usually occupy the para-position with reference to each other. Accordingly, if the para-position is 1.4, the formula of ordinary quinone is—

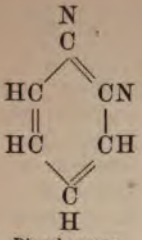


$= \quad C_6H_4O_2$.

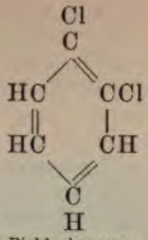
All quinones are supposed to be similarly constituted, though it is still a question whether all quinones are para-compounds. Certain experiments seem to indicate that there are quinones which belong to the meta-series.

Azo- and Diazo-Bodies.—These bodies, as their names imply, are nitrogen derivatives. They are derived from benzene and its homologues by the replacement of hydrogen by nitrogen. We shall consider those which are derived from benzene, as the others are very closely related to these, and will be understood if these are. The diazo-derivatives of benzene are obtained from the salts of anilin or amidobenzene, $C_6H_5.NH_2$, by the action of nitrous acid. Thus anilin nitrate, $C_6H_5.NH_2.HNO_3$, yields diazobenzene nitrate; anilin sulphate, $(C_6H_5.NH_2)_2.H_2SO_4$, yields diazobenzene sulphate, etc.

If we consider simply the empirical formulas of the salts of diazobenzene thus obtained, we shall find that they differ from the anilin salts in containing $C_6H_4N_2$ in the place of $C_6H_5NH_2$. The salts consist of the acids plus this group. Thus the nitrate is $C_6H_4N_2.HNO_3$; the sulphate is $C_6H_4N_2.H_2SO_4$, etc. These formulas are not supposed, however, to represent the constitution of the salts. If the group $C_6H_4N_2$ actually existed in these diazo-bodies, it is plain that they would be bi-substitution products, that is to say, two hydrogen atoms of benzene would be replaced by two nitrogen atoms. It was at first supposed that each of these nitrogen atoms played the part of a monovalent element, and the diazo-compounds were looked upon as analogous to bichlorbenzene, binitrobenzene, etc., thus:—



Diazobenzene.



Bichlorbenzene.

It was soon found, however, that, when the diazo-bodies were decomposed, they almost always yielded derivatives of benzene in which the group C_6H_5 was undoubtedly present. Thus the following decompositions of diazobenzene sulphate yield, in each case, a derivative containing C_6H_5:—

When boiled with alcohol, the products are benzene, nitrogen, and sulphuric acid—

$$\frac{C_6H_5.N_2.HSO_4}{H \qquad H} \quad \text{yield} \quad \begin{array}{r|c|l} C_6H_5 & N_2 & HSO_4 \\ H & & H \end{array}.$$

When boiled with water, the products are phenole, nitrogen, and sulphuric acid—

$$\frac{C_6H_5.N_2.HSO_4}{OH \qquad H} \quad \text{yield} \quad \begin{array}{r|c|l} C_6H_5 & N_2 & HSO_4 \\ OH & & H \end{array}.$$

When treated with hydriodic acid, the products are iodbenzene, nitrogen, and sulphuric acid—

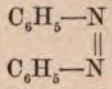
$$\frac{C_6H_5.N_2.HSO_4}{I \qquad H} \quad \text{yield} \quad \begin{array}{r|c|l} C_6H_5 & N_2 & HSO_4 \\ I & & H \end{array}.$$

Other reactions indicate as well that the group C_6H_5 is present in the diazo-compounds. But, if this group is present, the two nitrogen atoms must form a monovalent group, or, at all events, they must be so combined that they can take the place of one hydrogen atom. Now, if two nitrogen atoms which have the same valence be combined, they must either form a neutral group with all its affinities satisfied, or a group which is at least bivalent. Such a bivalent group would be formed, for instance, if two nitrogen atoms were to be united by means of two affinities each, thus, $—N{=}N—$. If this group should replace one hydrogen atom of benzene, the constitution of the resulting compound would be $C_6H_5—N{=}N—$. Such a compound would be unsaturated. No compound of the formula $C_6H_5N_2$ has been obtained, but all the derivatives of diazobenzene can be explained on the supposition that they are derived from the compound $C_6H_5—N{=}N—$. Griess, who discovered the diazo- and azo-compounds, and has given a great deal of time to their study, has described a body of the formula $C_6H_4N_2$, which he calls diazobenzene. If this body really exists, the conclusion above drawn concerning the presence of the group C_6H_5 in diazo-bodies would be weakened; but there seems to be just cause to doubt its existence.

Accepting the group $C_6H_5—N{=}N—$ as the foundation of the diazo-compounds, these may be formulated as follows:—

$C_6H_5—N{=}N—Br$,	diazobenzene bromide,
$C_6H_5—N{=}N—NO_3$,	diazobenzene nitrate,
$C_6H_5—N{=}N—HSO_4$,	diazobenzene sulphate,
$C_6H_5—N{=}N—OK$,	diazobenzene potassa,
$C_6H_5—N{=}N—NH(C_6H_5)$	diazobenzene diamidobenzene.

Azobenzene is formed by the reduction of nitrobenzene. Its formula is $C_{12}H_{10}N_2$. As nitrobenzene contains the group C_6H_5 combined with N, we can assume that azobenzene consists of two such groups $C_6H_5—N{=}$. If these combine in the simplest manner, we would have the formula

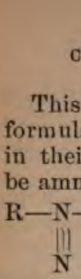


$$\begin{array}{r} C_6H_5—N \\ \| \\ C_6H_5—N \end{array}$$

, expressing the constitution of azobenzene. This is the formula which is now generally adopted.

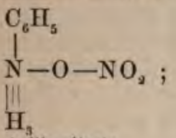
According to this, the azo-compounds are very closely related to the diazo-compounds. Both contain the group $—N{=}N—$ in combination with C_6H_5. In reality, the azo-compounds differ very much in their chemical conduct from the diazo-compounds. The decompositions which they undergo take place in a manner entirely different from that already noticed as characterizing the decomposition of diazo-compounds.

This difference has led some chemists to abandon the formulas above given for the diazo-compounds, proposing in their place others. The compounds are supposed to be ammonium compounds of the general formula—



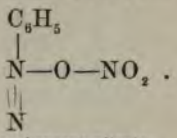
$$\begin{array}{c}R-N-R'\\ \|\!|\\ N\end{array}$$

. They contain one quinquivalent and one trivalent nitrogen atom. The relation between anilin nitrate and diazobenzene nitrate is shown thus:—



$$\begin{array}{l}C_6H_5\\ |\\ N-O-NO_2\ ;\\ \|\!|\\ H_3\end{array}$$

Anilin nitrate.



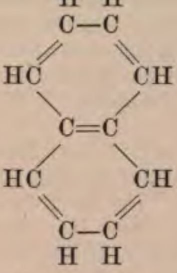
$$\begin{array}{l}C_6H_5\\ |\\ N-O-NO_2\ .\\ \|\!|\\ N\end{array}$$

Diazobenzene nitrate.

It remains to be determined, by future experiments, which of the formulas for diazo-compounds is correct. Up to the present there exist no good proofs of either.

NAPHTHALENE DERIVATIVES.

The hydrocarbon naphthalene has the formula $C_{10}H_8$. It is considered as being formed by the union of two benzene nuclei, and as having the constitution expressed by the formula—

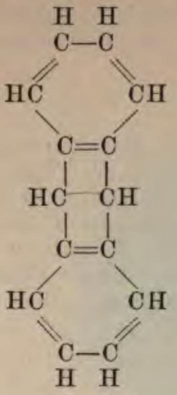


This formula is deduced from the following facts: There is a derivative of naphthalene known as dichlornaphthoquinone, which has the formula $C_{10}H_4Cl_2O_2$. When this substance is oxidized, it yields phthalic acid, which is a bi-substitution product of benzene. We see thus that those carbon atoms in dichlornaphthoquinone which are not in combination with chlorine form a benzene nucleus, so that we might write the formula of the compound $C_6H_4.C_4Cl_2O_2$. This formula does not tell us in what manner the atoms $C_4Cl_2O_2$ are united, but, by the aid of another experiment, this can be determined.

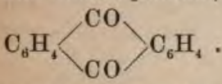
When dichlornaphthoquinone (the same substance used in the preceding experiment) is treated with phosphorus pentachloride, it is converted into pentachlornaphthalene, the formula of which, according to what was said above, is $C_6H_3Cl.C_4Cl_4$. By analogy, we would expect this compound by oxidation to yield monochlorphthalic acid; it, however, yields tetrachlorphthalic acid. This shows that the four carbon atoms which are in combination with chlorine form part of a benzene nucleus, as well as the other carbon atoms of naphthalene. It is thus proved that in naphthalene there are two benzene nuclei. The only formula which agrees with this fact is the one above given.

The derivatives of naphthalene resemble those of benzene, and much that has been said concerning this latter would hold good in regard to the former. All the hydrogen atoms of naphthalene may be replaced by substituting groups or elements, and thus, as will be readily seen, a large number of substitution products may be obtained. The possibilities for instances of isomerism are greater in the case of naphthalene than in the case of benzene, but the principles governing the matter of isomerism are essentially the same as those which we have already considered in connection with the isomeric substitution products of benzene.

Anthracene Derivatives.—Anthracene, like naphthalene and benzene, is the mother-substance of a large group of compounds. Its formula is $C_{14}H_{10}$. In regard to its constitution, the view is now commonly held that it consists of two benzene nuclei, C_6H_4, held together by means of the group $H\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}H$, each carbon atom of which is united with both benzene nuclei, thus:—

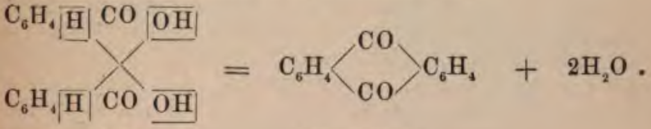


This formula shows the relation between anthracene and anthraquinone, which latter compound appears to be



$$C_6H_4\left\langle\begin{matrix}CO\\ \\CO\end{matrix}\right\rangle C_6H_4 .$$

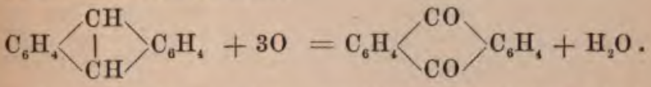
The latter formula best explains the formation of anthraquinone from benzoic acid, and the formation of benzoic acid from anthraquinone. The former transformation is represented thus:—



$$\begin{matrix}C_6H_4\boxed{H}\ CO\ \boxed{OH}\\ \times\\ C_6H_4\boxed{H}\ CO\ \boxed{OH}\end{matrix} = C_6H_4\left\langle\begin{matrix}CO\\ \\CO\end{matrix}\right\rangle C_6H_4 + 2H_2O .$$

2 molecules Benzoic acid. Anthraquinone.

The formation of anthraquinone from anthracene would be then represented thus:—



$$C_6H_4\left\langle\begin{matrix}CH\\ |\\CH\end{matrix}\right\rangle C_6H_4 + 3O = C_6H_4\left\langle\begin{matrix}CO\\ \\CO\end{matrix}\right\rangle C_6H_4 + H_2O .$$

According to these interpretations, anthraquinone is a double acetone. It has been suggested, further, that all quinones are nothing but double acetones. (See Quinones, p. 221.)

The derivatives of anthracene resemble in some respects those of naphthalene and of benzene. It will be seen, however, that some differences must exist between them.

Other hydrocarbons allied to naphthalene are pyrene, chrysene, and phenanthrene. These have not been investigated very fully as compared with naphthalene and anthracene themselves. All of these three undoubtedly contain benzene nuclei as essential parts of their molecules, but there is still some doubt in regard to the manner in which these nuclei are united.

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ERRATA.

Page 84, line 2 from bottom, omit "nitric acid, $\overset{V}{N}\overset{IV}{O_2}(\overset{I}{OH})$."

Page 84, bottom line, omit "nitrates and."

Page 191, middle of page, *read* "A third variety of heptane" for "A third variety of hexane."

Page 217, middle of page, after the sentence ending "1 and 2 in this formula," insert "these groups being considered in their relations to the upper benzene nucleus."

Page 227, the two middle carbon atoms in the formula for anthracene should be connected by a line.

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